UK Hydrocarbon Network

Annual Report for 2012

Report for Defra and the Devolved Administrations

Ricardo-AEA/R/ED47833 and ED46645
Issue Number 1
Date 25/06/2013

Customer:

Defra and the Devolved Administrations

Customer reference:

RMP 5504/5505

Confidentiality, copyright & reproduction:

Ricardo-AEA reference:

Ref: ED47833 and ED46645- Issue Number 1

Contact:

James Dernie
Ricardo-AEA Ltd
Gemini Building, Harwell, Didcot, OX11 0QR
t: 01235 75 6434
e: james.dernie@ricardo-aea.com

Ricardo-AEA is certificated to ISO9001 and ISO14001

Author:

James Dernie, Peter Dumitrean

Approved By:

Steve Telling

Date:

25 June 2013

Signed:

Executive summary

This report provides a summary of the site management and data produced in 2012 by the UK Hydrocarbon monitoring network.

This network comprises automatic and non-automatic systems to measure benzene. 1,3-butadiene and 29 ozone precursor substances are also measured using the automatic system. Since August 2012, formaldehyde and acetaldehyde have been measured at 5 sites as part of a two year pilot study.

The report includes an introduction to the network, the history of monitoring and the reasons for monitoring these pollutants. Section 2 provides detailed information on the sites currently operating and changes to the network during 2012. In section 3 and Appendix 2, summary data is presented and analysed, including a review of the long-term trends and a description of issues that have affected data capture or data quality. The report also includes a summary of the quality assurance and quality control procedures in sections 2 and 4 and an update on future changes in section 5.

The mean data capture for benzene measured by the non-automatic hydrocarbon sites in 2012 was 82.7%. It is important to note that some sites were removed and others installed during the calendar year. The data capture for sites running between January and December 2012 was 94.8%. The annual mean concentration across all non-automatic measurement sites in the UK was 0.82 $\mu g\ m^{-3}$ and the highest annual mean concentration for a single site was 1.97 $\mu g\ m^{-3}$ measured at Grangemouth. The mean data capture for benzene measured by the automatic hydrocarbon network in 2012 was 89.9% and the highest annual mean measurement for a single site was 1.4 $\mu g.m^{-3}$ at London Marylebone Road. The annual mean across all automatic measurement sites in the UK was 0.65 $\mu g.m^{-3}$.

In 2012 none of the automatic and non-automatic monitoring sites in the UK exceeded the 5 $\mu g\ m^{-3}$ annual mean Limit Value for benzene set out in Directive 2008/50/EC[1], hereafter referred to as ‘the Directive’. All sites measured an annual mean that was less than the Lower Assessment Threshold of 2 $\mu g\ m^{-3}$ defined within the directive.

[1] EC(2008). Directive 2008/50/EC The European Parliament and the Council of May 2008 on ambient air quality and cleaner air for Europe.

Table of contents

1 Introduction

This report provides a summary of the site management and data produced in 2012 by the UK Hydrocarbon monitoring network.

This network comprises automatic and non-automatic systems to measure benzene. 1,3-butadiene and 29 ozone precursor substances are also measured using the automatic system. Since August 2012, formaldehyde and acetaldehyde have been measured at 5 sites as part of a two year pilot study.

The network has been managed and quality controlled by AEA until 8th November 2012, from 9th November 2012, Ricardo-AEA.

All hydrocarbon network instruments are collocated at AURN (Automatic Urban and Rural Network) sites with the exception of Bury Roadside, this site was de-affiliated from the AURN on 6th September 2012 and is currently due to be relocated during 2013. The 40 non automatic sites have all been assessed with respect to the macroscale and microscale siting criteria in the Directive. The initial assessment indicates that all of the hydrocarbon network sites comply with the Directive, with the exception of Bury Roadside, Bristol Old Market and Leicester Centre. Bury Roadside and Bristol Old Market are believed to be too close to major road junctions to be representative of the local area, and additionally, the Bury Roadside site is too far from the carriageway to be a 'traffic' site. Leicester centre is surrounded by tall buildings in close proximity to the inlet.

The number and location of sites in the network are based upon a preliminary assessment against the sampling requirements in Annex V of the Air Quality Directive, undertaken in 2006[2]. A monitoring regime assessment of the number and location of monitoring sites in each Member State is required to be undertaken every 5 years, the UK carried out this reassessment for the hydrocarbons network in 2011. The automatic instruments will remain at their current locations. Changes to the location of non-automatic samplers are detailed in Section 2.1.

The information and data presented in this report are correct at the time of publication, however, it is possible that data may be rescaled or deleted from the dataset if future audits and calibrations identify a need to change the data. Latest data can always be accessed at http://uk-air.defra.gov.uk/.

1.1 Pollutant Sources and Impacts

Benzene has a variety of sources[3], but primarily arises from domestic and industrial combustion and road transport. It is a recognised human carcinogen that attacks the genetic material and, as such, no absolutely safe level can be specified in ambient air. Studies in workers exposed to high levels have shown an excessive risk of leukaemia.

1,3-butadiene is emitted from combustion of petrol. Motor vehicles and other machinery are the dominant sources, but it is also emitted from some processes, such as production of synthetic rubber for tyres. 1,3-butadiene is also a recognised genotoxic human carcinogen, as such, no absolutely safe level can be specified in ambient air. The health effect of most

[2] Defra (2013) UK Air Quality Monitoring Strategy. Compliance Assessment under the Ambient Air Quality Directive 2008/50/EC. Department of the Environment, Food Rural Affairs in partnership with the Scottish Executive, the Welsh Assembly Government and the Department of the Environment Northern Ireland. The Stationery Office, London.(under preparation).

[3] The Air Quality Strategy for England, Scotland, Wales and Northern Ireland (Volume 1), Department for Environment, Food and Rural Affairs in partnership with the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland, July 2007

concern is the induction of cancer of the lymphoid system and blood–forming tissues, lymphoma and leukaemia.

1.2 Network background and methods

The UK Hydrocarbon Network exists within the framework of Defra's Atmosphere and Local Environment Programme. This aims to determine the magnitude of sources and effects of air pollutants on human health and the environment, and to comply with national and EU legislation.

1.2.1 Non-Automatic Hydrocarbon Sites

The Non-Automatic Hydrocarbon Sites started operation in 2001, measuring benzene and 1,3-butadiene. It currently produces measurements as nominal fortnightly averages at 34 sites. The network was reviewed in 2007 and 1,3-butadiene monitoring was discontinued due to the measurement of very low concentrations. During 2012 measurements have been made at 41 sites as a result of changes to the network (Appendix 1).

The benzene monitoring method involves drawing ambient air at a controlled rate (nominally 10 ml/min) alternately through two tubes (A and B) containing a carbon based sorbent (Carbopack X). Each tube samples alternately at 10 ml/min for 8 minute periods for a nominal two week period. A designated local site operator manually changes the tubes and returns these to Ricardo-AEA, on completion of the sampling period. The tubes are then sent to the laboratory for subsequent analysis for benzene by gas chromatography-mass spectrometry. The sampling period and sample flow rate are important such that enough benzene is captured onto the sorbent to enable fully quantifiable analysis, but not too much that there is breakthrough of the sample. This dual sample tube controlled flow pump unit uses a method described in EN 14662:2005, 'Ambient air quality – Standard method for measurement of benzene concentrations' by Martin et al[4], and validated by Quincey et al[5].

1.2.2 Automatic Hydrocarbon Sites

Automated thermal desorption with in situ gas chromatography and FID detection is used to measure hourly hydrocarbon concentrations. During 2012, hydrocarbons at all sites were measured using automatic Perkin Elmer Ozone Precursor Analysers. A known volume of air is dried and drawn through a cold trap, which contains adsorbent material. The cold trap is held at about -30^{o}C to ensure that all the ozone precursor target analytes are retained. Following a 40 minute period of sampling, components are desorbed from the cold trap and are transferred to the capillary column where they are separated using gas-chromatography and subsequently detected by a flame ionising detector. The analyser is calibrated using an on-site multi-component gas mixture.

Automatic hourly measurements of speciated hydrocarbons, made using advanced automatic gas chromatography, started in the UK in 1991. By 1995, monitoring had expanded considerably with the formation of a 13-site dedicated network measuring 26 species continuously at urban, industrial and rural locations. Over the following years, the number of sites was reduced. In 2012 there were four sites, measuring the following species by automatic gas chromatographs:

---

[4] Martin *et al*, 2003. Studies using the sorbent Carbopack X for measuring environmental benzene with Perkin-Elmer-type pumped and diffusive samplers. Atmospheric Environment, **37**, (7), 871-879

[5] http://www.airquality.co.uk/archive/reports/cat05/0407061411_btex_npl_pilot_final.pdf

Table 1 Species measured by the Automatic chromatographs

Pollutant	Pollutant	Pollutant
1,2,3-trimethylbenzene	ethane	n-heptane
1,2,4-trimethylbenzene	ethene	n-hexane
1,3,5-trimethylbenzene	ethylbenzene	n-octane
1,3-butadiene	ethyne (acetylene)	n-pentane
1-butene	iso-butane (I-butane)	o-xylene
1-pentene	iso-octane	propane
2-methylpentane	iso-pentane	propene
3-methylpentane	isoprene	toluene
benzene	m+p-xylene	trans-2-butene
cis-2-butene	methylpentane	trans-2-pentene
cis-2-pentene	n-butane	

1.2.3 2 Year Aldehyde Pilot Study

In order to reduce the burden on fossil fuels and to help mitigate climate change, the EU Government introduced the Renewable Energy Directive (FQD, 98/70/EC). Obligations under articles 7a to 7e requires member states to implemement a strategy to increase renewable fuel use for transport. The UK introduced the Renewables Transport Fuel Obligation (RTFO). Bioethanol is a renewable fuel that can be added to conventional petrol for use in modern conventional engines.

In 2011, the UK Air Quality Expert Group (AQEG) provided advice to Defra and the devolved administrations suggesting the potential for increases in aldehyde emissions following the introduction of bioethanol to conventional petroleum used in road transport [6]. The advice suggests that low blends ≤5% will significantly increase emission of acetaldehyde from motor vehicle exhaust. For higher strength blends >5%, an increase of formaldehyde may also be seen.

In response to this advice, Defra requested a two year pilot study of airborne aldehyde emissions to be carried out.

The aldehyde monitoring method involves drawing ambient air at a rate nominally 700 ml/min through a packed bed silica tube containing dinitriphenylhydrazine(DNPH). Sampling is for a 24hr period, twice a week; Tuesday and Thursday. The tubes are sent to the laboratory for acetaldehyde and formaldehyde analysis by high performance liquid chromatography (HPLC). The exposure period and flow rate is selected to optimise capture onto the sorbent and minimise breakthrough. There is not yet a reference method for measuring aldehydes and the bespoke sampler has been built by Ricardo-AEA specifically for the DNPH tubes.

[6] AQEG, 2011. Road Transport Biofuels: Impact on UK Air Quality. Advice note prepared for Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Assembly Government; and Department of the Environment in Northern Ireland

Regulatory background

1.2.4 UK Air Quality Objectives

The Air Quality Strategy for England, Scotland, Wales and Northern Ireland, (July 2007) sets out the UK Air Quality Objectives for benzene and 1,3-butadiene:

Table 2 UK Air Quality Objectives.

Pollutant	Applicable to	Concentration	Measured As	To be achieved by
Benzene	All authorities	16.25 µg m^{-3}	Running annual mean	31 December 2003
	England and Wales Only	5.00 µg m^{-3}	Annual mean	31 December 2010
	Scotland and N. Ireland	3.25 µg m^{-3}	Running annual mean	31 December 2010
1,3-Butadiene	All authorities	2.25 µg m^{-3}	Running annual mean	31 December 2003

1.2.5 European Limit Value

Hydrocarbons are also governed by Directive 2008/E50/EC of the European Parliament and of the Council of 21 May 2008, on ambient air quality and cleaner air for Europe (the Directive). The Directive sets a limit value for annual mean benzene concentrations across Member States.

Table 3 European Limit Value and Assessment Thresholds

Threshold	Concentration	Measured as
Limit Value	5µg m^{-3}	Annual mean
Upper assessment threshold	3.5µg m^{-3}	Annual mean
Lower assessment threshold	2µg m^{-3}	Annual mean

The limit value for the protection of human health for benzene is 5 µg/m^3 as a calendar year mean, to be achieved by 1st January 2010. The determination of requirements for assessment of concentrations of benzene in ambient air is between 3.5 µg/m^3 (70% of limit value) and 2 µg/m^3 (40% of limit value) as upper and lower assessment threshold respectively.

The Data Quality Objective for the measurement uncertainty is ±25% with a minimum data capture of 90%. The minimum time coverage is 35% (distributed over the year) for urban background and traffic sites and 90% for industrial sites.

Annex X of the Directive lists 31 other Volatile Organic Compounds (VOCs) which are ozone precursors and which are recommended to be measured in urban or suburban areas to support the understanding of ozone formation. With the exception of formaldehyde and total non-methane hydrocarbons, these VOCs are all measured by the automatic hydrocarbon instruments and are listed in section 1. Neither data quality objectives nor limit values are given for measurement of these species, however, Defra have specified that all other VOC compounds have a minimum data capture target of 50%.

2 Site Management

2.1 Network sites during 2012

2.1.1 Non-Automatic Hydrocarbon Network

The sites in the Non-Automatic Hydrocarbon Network are shown in Figure 1. Table 4 lists the sites and the Local Site Operators.

Figure 1 Map of Non-Automatic Hydrocarbon Network sites in 2012

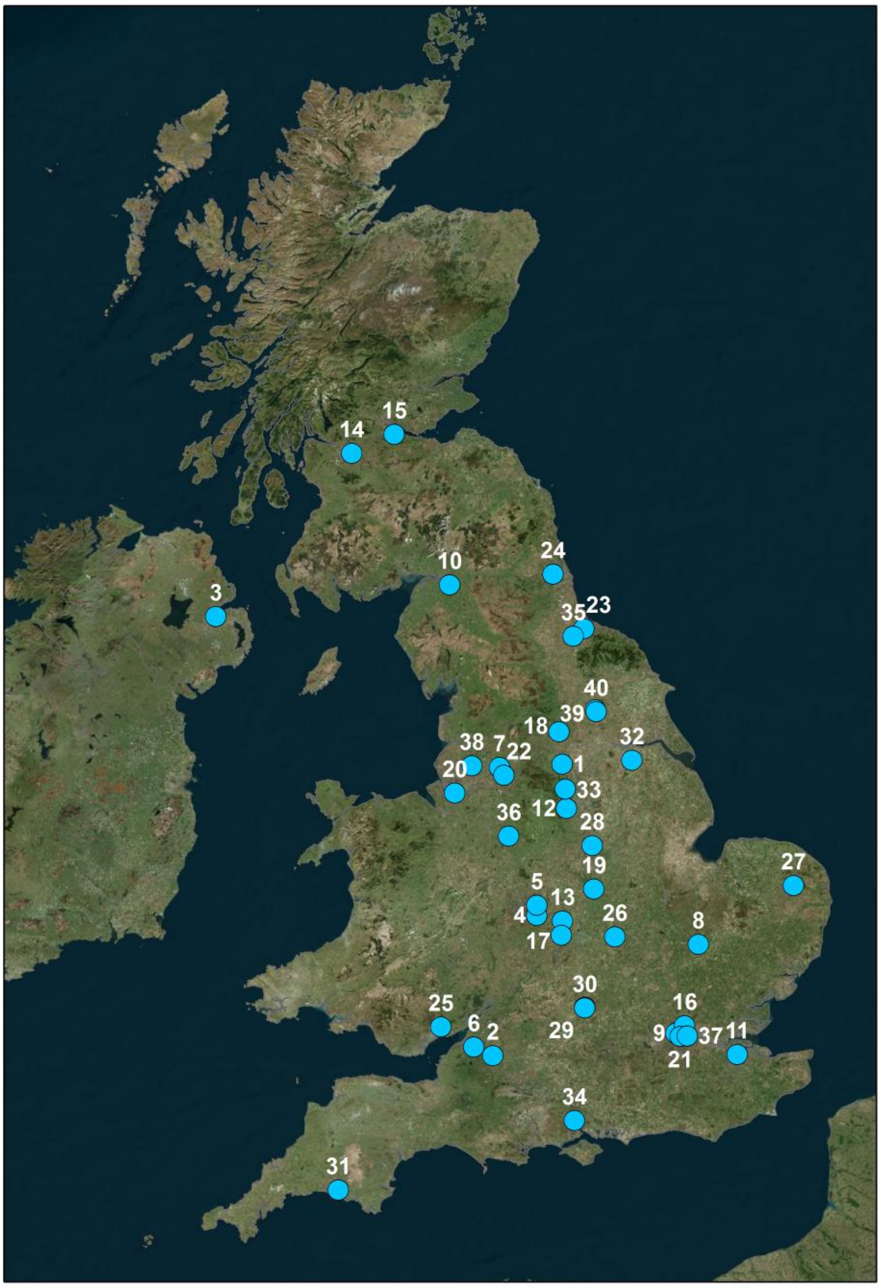


Table 4 Non-Automatic Hydrocarbon Network sites in 2012.

	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
1	Barnsley Gawber	Urban Background	Yorkshire & Humberside	432529, 407472	Barnsley Council
2	Bath Roadside	Urban Traffic	South West	375882, 166096	Bath & North Somerset Council
3	Belfast Centre	Urban Background	Belfast Urban Area	333900, 374400	Belfast City Council
4	Birmingham Acocks Green	Urban Background	West Midlands Urban Area	411654, 282146	Birmingham City Council
5	Birmingham Tyburn Roadside	Urban Traffic	West Midlands Urban Area	411556, 290456	AECOM
6	Bristol Old Market	Urban Traffic	Bristol Urban Area	359570, 173173	Bristol City Council
7	Bury Roadside	Urban Traffic	Greater Manchester Urban Area	380922, 404772	Bury Metropolitan Council
8	Cambridge Roadside	Urban Traffic	Eastern	545248, 258155	Cambridge Council
9	Camden Kerbside	Urban Traffic	Greater London Urban Area	526640, 184433	AEA / Ricardo-AEA
10	Carlisle Roadside	Urban Traffic	North West & Merseyside	339442, 555956	Carlisle Council
11	Chatham Centre Roadside	Urban Traffic	South East	577435, 166993	Medway Council
12	Chesterfield	Urban Background	East Midlands	436351, 370682	Chesterfield Council
13	Coventry Memorial Park	Urban Background	Coventry/Bedworth	432801, 277340	Coventry City Council
14	Glasgow Kerbside	Urban Traffic	Glasgow Urban Area	258708, 665200	AEA / Ricardo-AEA
15	Grangemouth	Urban Industrial	Central Scotland	293837, 681035	Falkirk Council
16	Haringey Roadside	Urban Traffic	Greater London Urban Area	533885, 190669	KCL / Ricardo-AEA
17	Leamington Spa	Urban Background	West Midlands	431932, 265743	Warwick District Council
18	Leeds Centre	Urban Background	West Yorkshire Urban Area	429976, 434268	Leeds City Council
19	Leicester Centre	Urban Background	Leicester Urban Area	458767, 304083	Leicester City Council
20	Liverpool Speke	Urban Background	Liverpool Urban Area	343860, 383598	Fabermaunsell/AECOM
21	London Bloomsbury	Urban Background	Greater London Urban Area	530107, 182041	Bureau Veritas / AEA / Ricardo AEA
22	Manchester Piccadilly	Urban Background	Greater Manchester Urban Area	384310, 398325	Manchester City Council
23	Middlesbrough	Urban Background	Teesside Urban Area	450480, 519632	Middlesbrough BC
24	Newcastle Centre	Urban Background	Tyneside	425016, 564940	Newcastle City Council
25	Newport	Urban Background	South Wales	33410, 189604	Newport City Council
26	Northampton*	Urban Background	East Midlands	476111, 264524	Northampton BC

	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
27	Norwich Lakenfields	Urban Background	Eastern	623637, 306940	Mark Leach
28	Nottingham Centre	Urban Background	Nottingham Urban Area	457420, 340050	Nottingham City Council
29	Oxford Centre Roadside	Urban Traffic	South East	451366, 206152	Oxford City Council
30	Oxford St Ebbes	Urban Background	South East	451225, 206009	Oxford City Council
31	Plymouth Centre	Urban Background	South West	247742, 54610	Plymouth City Council
32	Scunthorpe Town	Urban Industrial	Yorkshire & Humberside	490338, 410836	North Lincs CBC
33	Sheffield Centre	Urban Background	Sheffield Urban Area	435134, 386885	Sheffield City Council
34	Southampton Centre	Urban Background	Southampton Urban Area	442565, 112255	Southampton City Council
35	Stockton-on-Tees - Eaglescliffe	Urban Traffic	North East	441620, 513673	Stockton on Tees BC
36	Stoke-on-Trent Centre	Urban Background	The Potteries	388348, 347894	City of Stoke on Trent Council
37	Tower Hamlets Roadside	Urban Traffic	Greater London	535927, 182218	Kings College, London
38	Wigan Centre	Urban Background	North West & Merseyside	357825, 406025	Wigan Metropolitan BC
39	York Bootham	Urban Backgorund	Yorkshire & Humberside	460024, 452768	City of York Council
40	York Fishergate	Urban Traffic	Yorkshire & Humberside	460744, 451033	City of York Council

*This site was temporarily moved to Northampton Kingsthorpe a few weeks before the sampler was removed.

As part of an ongoing investigation, there were also pumped samplers operating at Marylebone Road from 2007 to January 2013, and at London Eltham from 2011until June 2012. These pumped samplers are not part of the Non-Automatic Network.

Further details on the sites can be found on the UK Automatic Urban and Rural Network Site Information Archive at http://uk-air.defra.gov.uk/

2.1.1 Automatic Hydrocarbon Network

The sites in the Automatic Hydrocarbon Network are shown in Figure 2.

Figure 2 Map of Automatic Network sites in 2012

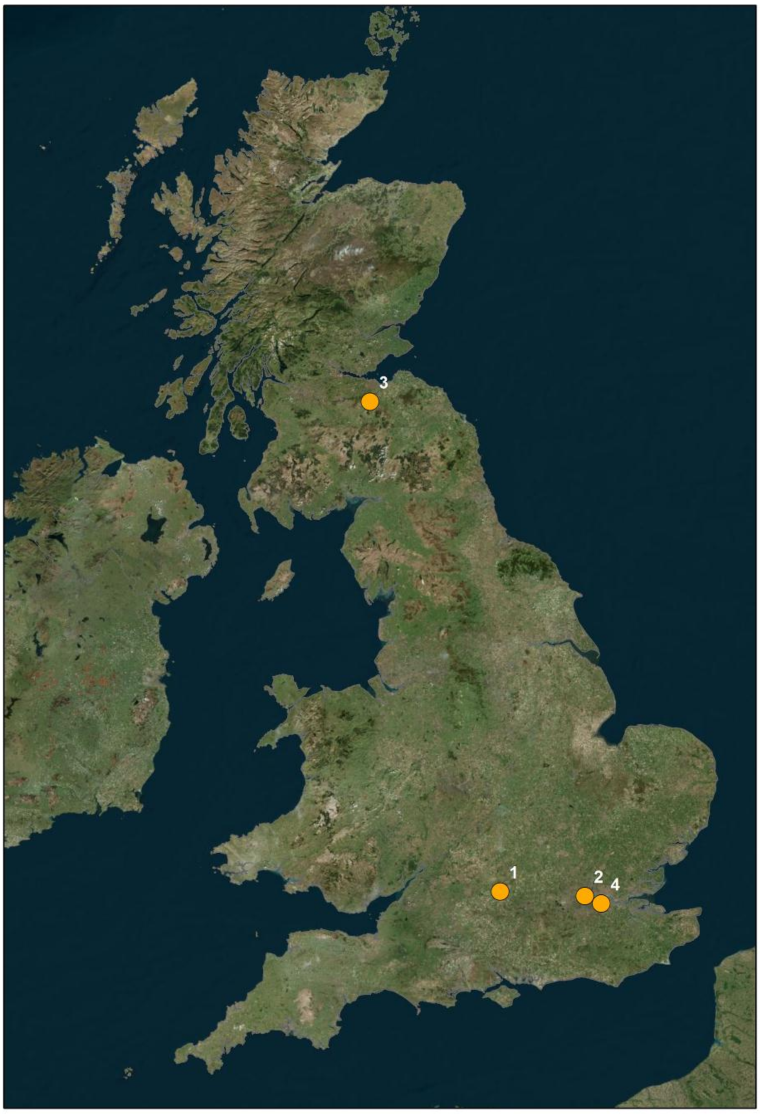


Table 5 Automatic Hydrocarbon Network sites in 2012.

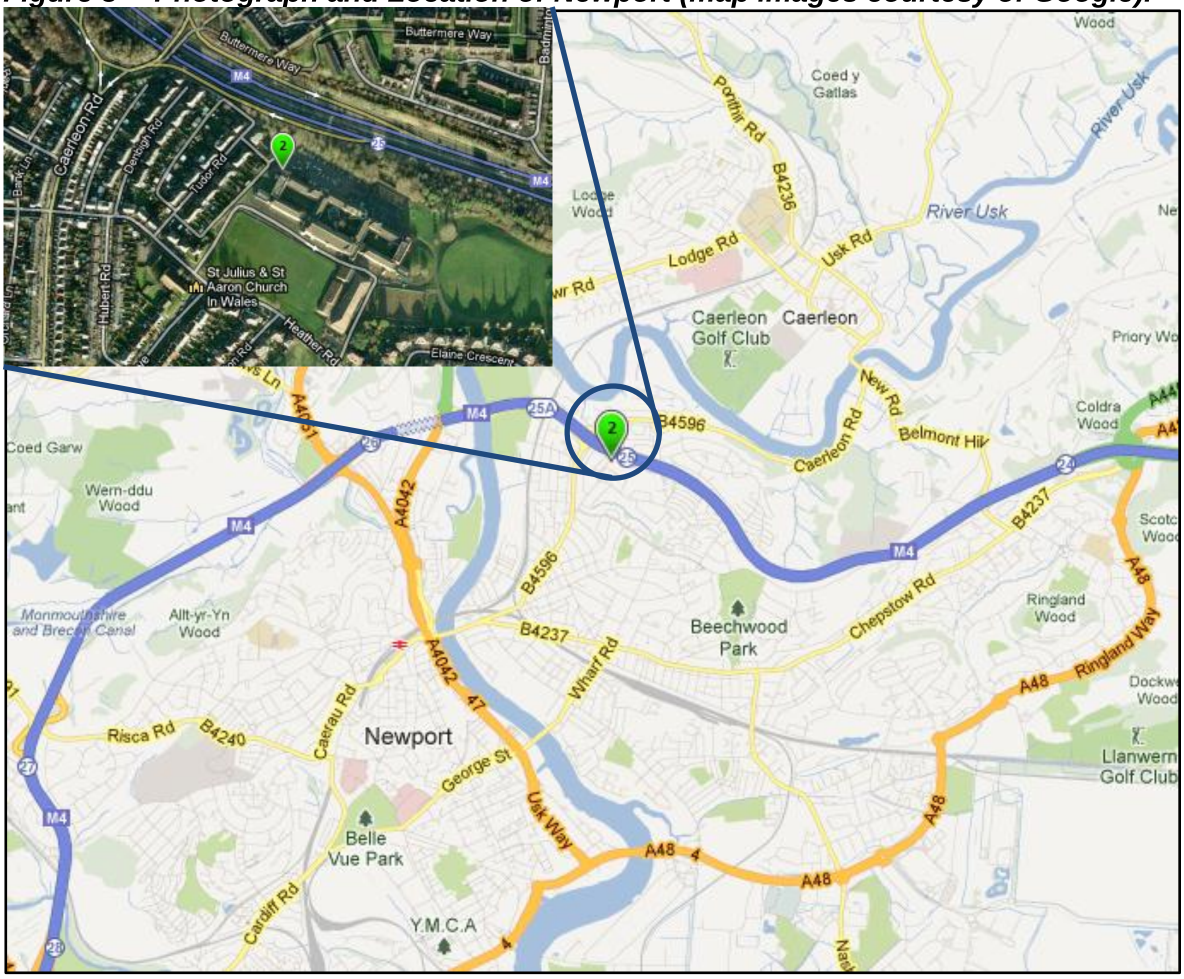
	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
1	Harwell	Rural Background	South West	446772, 186020	AEA/ Ricardo-AEA
2	Marylebone Road	Urban Traffic	Greater London Urban Area	528120, 182000	KCL
3	Auchencorth Moss	Rural Background	Scotland	322050, 656250	CEH
4	London Eltham	Suburban Background	Greater London Urban Area	543978, 174668	Greenwich Borough Council

2.1 Additional Sites in 2012

2.1.1 Newport

The monitoring regime assessment[7] identified that the Plymouth Centre monitoring site was not required for either compliance reporting or for the purposes of modelling. The report also identified that an additional site in South Wales was required for compliance with the directive. The Newport AURN site at St Julians School (Figure 3) was identified as an ideal location for the additional site and the benzene sampler from Plymouth Centre was relocated on 1st October 2012 and installed at Newport on 31st November 2012.

Figure 3 Photograph and Location of Newport (map images courtesy of Google).



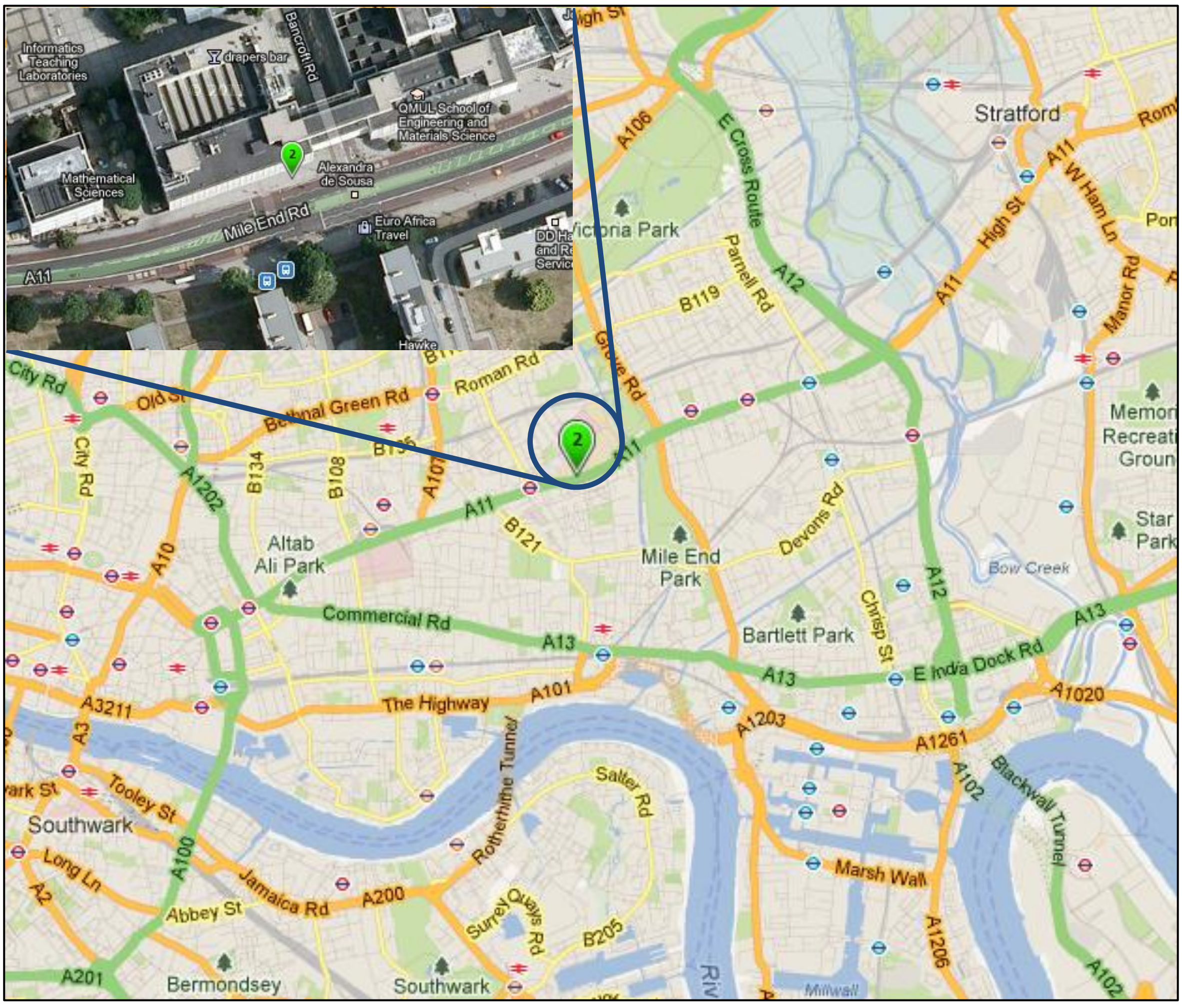
---

7 Defra (2013) UK Air Quality Monitoring Strategy. Compliance Assessment under the Ambient Air Quality Directive 2008/50/EC. Department of the Environment, Food Rural Affairs in partnership with the Scottish Executive, the Welsh Assembly Government and the Department of the Environment Northern Ireland. The Stationery Office, London.(under preparation).

2.1.2 Tower Hamlets Roadside

The review of the network recommended that the Bristol Old Market site was not required for either compliance or modelling and identified that an additional roadside site in London was required for modelling. The Tower Hamlets Roadside AURN site (Figure 4) was identified as an ideal location and the sampler was removed from Bristol Old Market on 3rd October 2012 and installed at Tower Hamlets Roadside 13th November 2012.

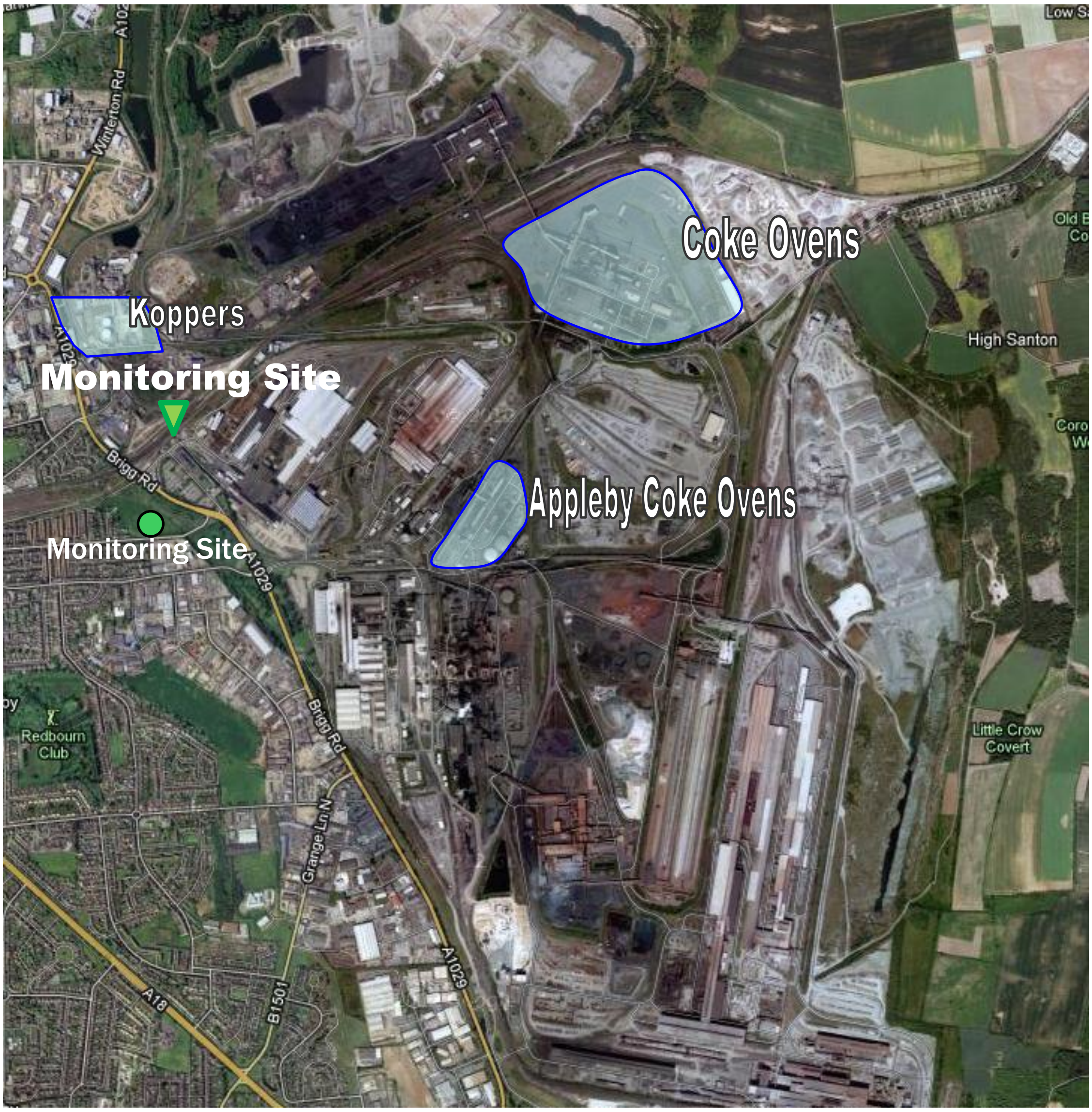
Figure 4 Photograph and location of Tower Hamlets Roadside (images courtesy of google)



2.1.3 Scunthorpe Town

The review of the network recommended that the Wigan Centre site was not required for compliance or modelling but that an additional site in North Lincolnshire was required for modelling. The Scunthorpe Town AURN site was identified as an ideal location. The sampler was removed from Wigan Centre on 9th October 2012 and installed at Scunthorpe Town on 6th November 2012. Scunthorpe Town is an industrial site with local industrial sources including Dawes Lane coke ovens, Appleby coke ovens and Koppers Tar/bitumen distillation site (Figure 5). Currently both the coke ovens are operational but the Koppers site is only used for storage purposes.

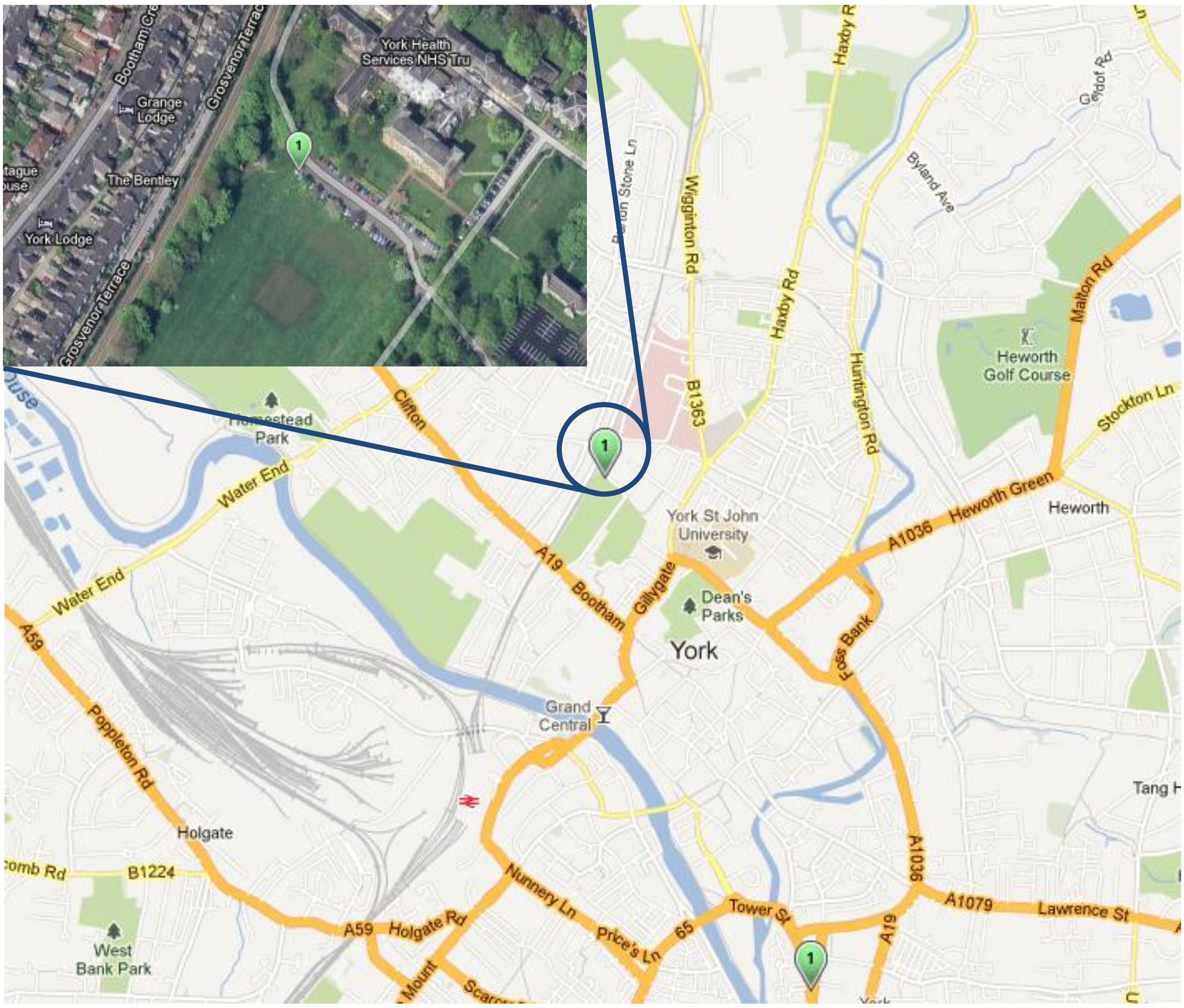
Figure 5 Photograph and location of Scunthorpe Town (images courtesy of google)



2.1.4 York Bootham

The Northampton site was moved to Northampton Kingsthorpe on 9th July 2012. The review of the network recommended that a site in Northampton was not required for benzene measurements for compliance or modelling. The sampler was removed from Northampton Kingsthorpe on 24th October 2012 and relocated to the York Bootham AURN site (Figure 6) on 5th November 2012 to provide an additional background site in Yorkshire and Humberside.

Figure 6 Photograph and location of York Bootham (images courtesy of google)



There were no other new sites installed during 2012. The London Eltham intercomparison stopped on 5th July 2012 and the London Marylebone Road intercomparison stopped in January 2013.The Coventry Memorial Park and Leicester Centre sites were also removed in early January 2013.

2.2 Equipment Maintenance and Audits

All non-automatic monitoring sites are visited by field engineers on a 6 monthly basis to calibrate the sampling flows and carry out routine maintenance of the equipment. The purpose of the audit and maintenance visits are to:

- Carry out a flow measurement and calibration using a low flow BIOS instrument (UKAS accredited)
- Ensure no blockages or leaks in the system
- Clean or replace dirty filters and inspect/replace the sample inlet
- Replace o-rings and leak test all connections
- Carry out electrical Portable Appliance Testing (annually)
- Review the site infrastructure and surroundings
- Review health and safety risks at the site
- Replace or refurbish non automatic sampler pumps

Non-Automatic Hydrocarbon benzene samplers were audited in October 2011, April 2012, October 2012 and April 2013. All of these measurements are used to calculate sample volumes for the 2012 data set by means of interpolation. The schedule and results of these visits can be seen in Appendix 1. The calibration data from these audits have been used to rescale the benzene concentrations during the ratification process. A copy of the certificate of accredited measurements is available in Appendix 3.

Automatic Hydrocarbon Network analysers are audited once each year, and in 2012 the audits took place between March and May:

- Auchencorth Moss 28th March 2012
- Harwell 16th April 2012
- London Marylebone Road 20th March 2012
- London Eltham 22nd March 2012

Following the audits the automatic monitoring sites are serviced by the Equipment Support Unit (Perkin Elmer) where the following routine tasks are undertaken:-

- Change automatic GC cold trap and clean the gas generators and detectors
- Carry out a gas calibration for the automatic analysers

3 Data and Data capture for 2012

3.1 Comparison with Limit Values and Objectives

The annual average concentration of benzene and 1,3 butadiene over the calendar year 2012 is given in **Error! Reference source not found.** and Table 7, alongside the data capture statistics. Data capture for sites where measurements started or finished during the year are calculated for the period that the equipment was operational.

Annual time weighted average concentrations at all sites were below the Limit Value of 5 µg/m^3 for benzene set by the European Ambient Air Quality Directive.

3.1.1 Non-Automatic Hydrocarbon site Statistics

Table 6 Benzene statistics 2012

Site	Annual Mean Benzene (µg/m^3)	Maximum Fortnightly Mean Benzene (µg/m^3)	Data capture (%)
Barnsley Gawber	0.45	1.0	88%
Bath Roadside	1.5	2.7	100%
Belfast Centre	0.55	1.5	100%
Birmingham Acocks Green	0.59	1.2	96%
Birmingham Tyburn Roadside	0.85	1.7	92%
Bristol Old Market	0.83	1.6	72%
Bury Roadside	0.72	1.6	100%
Cambridge Roadside	0.74	1.4	96%
Camden Kerbside	1.1	2.1	100%
Carlisle Roadside	0.74	1.7	89%
Chatham Roadside	0.84	1.4	97%
Chesterfield Roadside	1.2	4.1	82%
Coventry Memorial Park	0.51	1.3	100%
Glasgow Kerbside	0.90	1.9	92%
Grangemouth	2.0	19	100%
Haringey Roadside	1.0	1.8	100%
Leamington Spa	0.63	1.7	96%
Leeds Centre	0.63	1.3	100%
Leicester Centre	0.63	1.4	100%
Liverpool Speke	0.76	1.5	76%
London Bloomsbury	0.73	2.0	100%
Manchester Piccadilly	0.73	1.5	95%
Middlesbrough	1.2	3.3	96%

Site	Annual Mean Benzene (µg/m^3)	Maximum Fortnightly Mean Benzene (µg/m^3)	Data capture (%)
Newcastle Centre	0.51	1.1	96%
Newport	0.73	1.1	17%*
Northampton	0.55	1.0	51%*
Northampton Kingsthorpe	0.32	0.42	27%*†
Norwich Lakenfields	0.60	1.3	96%
Nottingham Centre	0.67	1.8	93%
Oxford Centre	0.63	1.6	96%
Oxford st Ebbes	0.56	1.4	87%
Plymouth Centre	0.57	1.2	75%*
Scunthorpe Town	1.2	1.8	13%*
Sheffield centre	0.65	1.6	100%
Southampton Centre	0.77	1.5	100%
Stockton-on-Tees Eaglescliffe	0.79	1.4	72%
Stoke-on-Trent Centre	0.79	1.6	100%
Tower Hamlets Roadside	1.4	1.7	15%*
Wigan Centre	0.58	1.8	75%*
York Bootham	1.0	1.4	13%*
York Fishergate	0.88	1.9	100%

*Site installed/removed during 2012
†Site moved to new location 'Northampton Kingsthorpe' (unit on wheels) prior to removal

During 2012, the following site faults and failures were recorded:

Barnsley Gawber

No sample flow was found at the routine audit on 31st October 2012. The sampler was replaced. 42 days lost due to lack of confidence in the flow used for sample volume calculations.

Birmingham Acocks Green*

One sample removed starting 17th July 2012, analytical result discrepancy. 14 Days were lost.

Birmingham Tyburn Roadside*

Two samples removed. The first starting on 14th February 2012, the second starting 17th July 2012, analytical result discrepancy. 28 days were lost in total.

*Note that it is possible that the LSO switched the tubes at the Birmingham sites on 17th July. It is not possible to determine which result is relevant to which sampler.

Cambridge Roadside

Sample starting on 17th October 2012 reported as zero mass. Data marked as not for dissemination. 14 days were lost.

Carlisle Roadside

Very low analytical results with no agreement, data marked as not for dissemination from 27th June 2012, 42 days were lost.

Chatham Centre Roadside

Low data from 5th January, Tube A and B discrepancy. Data marked as not for dissemination. 12 days were lost.

Chesterfield Roadside

Data from 25th October 2012 marked as not for dissemination following poor data, a site visit on 20th December 2012 showed a low flow error from the previous audit. 70 days were lost.

Glasgow Kerbside

Power cut resulting in loss of data from 26th October 2012. 28 Days were lost.

Leamington Spa

Data from 26th January 2012 removed, large discrepancy between tube results. 14 days lost.

Liverpool Speke

Data from 4th January large discrepancy between tube results. 15 days lost. Data from 15th February large discrepancy between tube results. 15 days lost. Sampler stuck on Tube A from 13th March, sampler replaced. 70 Days lost.

Manchester Piccadilly

Sampler removed on 13th December 2011, new sampler not installed until 11th January 2012. 11.5 Days lost. It had not been possible to replace the sampler before Christmans/New Year.

Middlesbrough

An analytical discrepancy between Tube A and B, the sample beginning 17th April 2012 was removed, 14 days data lost.

Newcastle Centre

Data for the sample beginning 8th February 2012 was removed, Tube mass unusually low, considered erroneous, 15 days lost.

Norwich Lakenfields

An analytical discrepancy between Tube A and B for the sample starting 18th April 2012, 14 days was lost.

Nottingham Centre

Removed data relevant to the sample from 28th November 2012. Discrepant analytical result and unusually high, considered erroneous. 15 days lost.

Oxford Centre Roadside

Data for 15th February 2012 onwards was lost, sampling tubes lost in the post from site.

Oxford St Ebbes

Data for 15th February 2012 onwards was lost, sampling tubes lost in the post from site. Data on 13th November 2012 removed, sample tube results unusually low, especially for a longer sampling period, this was considered erroneous. 21 days was lost.

Stockton-on-Tees Eaglescliffe

Data from 24th May 2012 removed, sampler partially stuck on one tube. Sample volume cannot be verified, 103 days were lost.

3.1.1 Automatic Hydrocarbon Network site Statistics

Table 7 Benzene and 1,3-butadiene Statistics

Site	Pollutant	Annual Mean ($\mu g/m^3$)	Maximum ($\mu g/m^3$)	Data capture
Harwell	Benzene	0.36	3.1	93%
	1,3-Butadiene	0.090	1.3	95%
Marylebone Road	Benzene	1.4	7.7	88%
	1,3-Butadiene	0.13	2.0	88%
Auchencorth Moss	Benzene	0.23	2.8	90%
	1,3-Butadiene	0.02	0.65	80%
London Eltham	Benzene	0.62	12	89%
	1,3-Butadiene	0.090	1.4	90%

Annual Mean concentrations for all measured hydrocarbons at all sites are given in Appendix 2.

Data capture is currently calculated based on the number of valid data points in the year. The calculation does not take into account any instrument downtime for planned services and maintenance or calibrations. It also does not take into account periods when no data are recorded because the ambient concentrations are less than the limit of detection. This is particularly significant at Auchencorth Moss, where concentrations of many pollutants are very low. In future years data which are reported to the European Commission will be required to include flags to identify data less than the detection limit, and these data will be included in the data capture calculation, so the reported data capture is likely to improve.

Harwell

Data capture for benzene and 1,3-butadiene was over 90 % for 2012. Data capture for some of the other hydrocarbons was lower due to co-eluting peaks and low ambient levels.

Marylebone Road

There were a number of power cuts and minor analyser problems throughout the year, usually lasting no more than a day each. In total approximately 20 days of data were lost.

Auchencorth Moss

There were a number of power cuts throughout the year, usually lasting no more than a day each. In total approximately 30 days of data were lost.

London Eltham

There was a fault with the compressor in August and 10 days of data were lost.

There was a leak in the helium supply in September and 7 days of data were lost.

The power supply tripped at the end of December, there was no access in order to reset it and 7 days of data were lost.

3.2 Concentration trends

3.2.1 Trends in 2012

Time series graphs for benzene and 1,3 butadiene are available in Appendix 4. The majority of Traffic Urban and Background Urban sites show a distinct trend with benzene concentrations highest in the winter months, and lowest around July to September. At Urban and Rural sites there tends to be a pattern of seasonal variation with higher levels during the winter when transport and energy emissions are higher, dispersion is generally poorer and photochemical removal is at a minimum. This trend is less evident at Industrial sites including Middlesbrough and Grangemouth, where the emissions from the industry are significant.

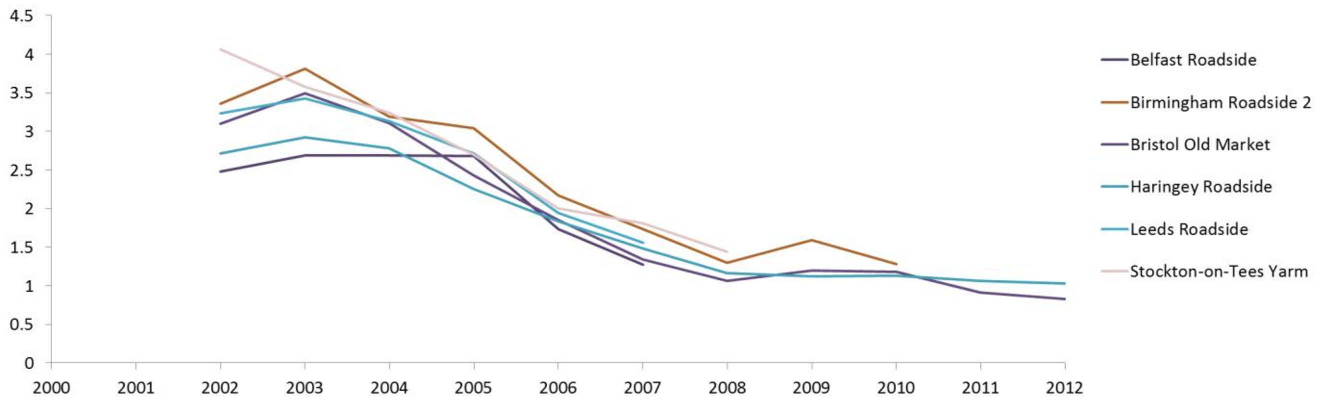
3.2.1 Long Term Trends

Figure 7 to 12 shows annual mean benzene concentrations at long running sites from the Non-Automatic Hydrocarbon Network. Concentrations at traffic sites have dropped significantly since the start of this network in 2002, but appear to be levelling out over the past couple of years. The exceptions are Bath Roadside and Chesterfield Roadside, both of which have seen increases over the past four years, fortnightly long term plots have been plotted (Figure 13 and 14) for additional resolution; these show that the same cannot be said for $NO_{x,}$ it's unclear why there are increases in benzene, there are no sampling faults, no step change has been recorded and all data have been fully validated by their respective network management teams.

Raised levels of benzene at Barnsley Gawber in 2005 were due to coal tar deposits uncovered by housing development that contained significant amounts of benzene[8] (NPL, 2006). Elevated levels at Middlesbrough during 2005 are considered a result of industrial activity in the area (Figure 12).

Long term Non-Automatic benzene annual mean trends.

Figure 7 - Long term Non-Automatic benzene annual mean trends.



[8] NPL, 2006. UK Non-Automatic Hydrocarbon Network: Annual report for 2005. NPL

Figure 8 - Long term Non-Automatic benzene annual mean trends.

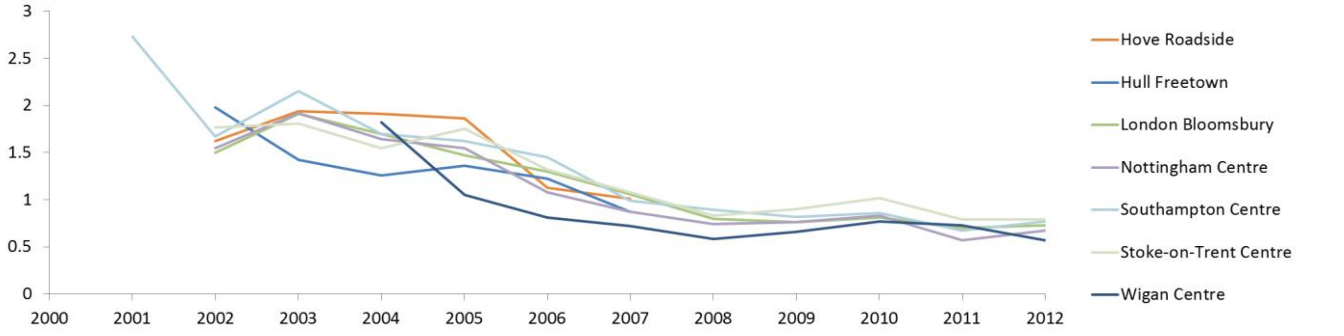


Figure 9 - Long term Non-Automatic benzene annual mean trends.

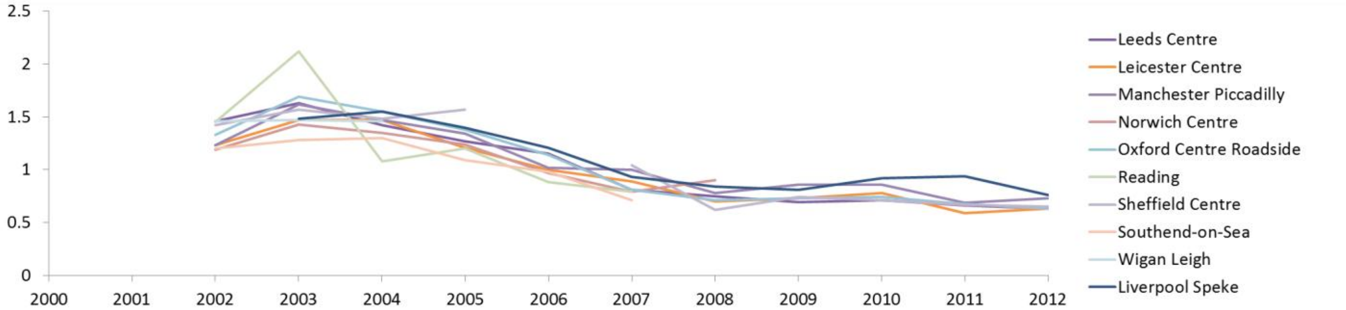


Figure 10 - Long term Non-Automatic benzene annual mean trends.

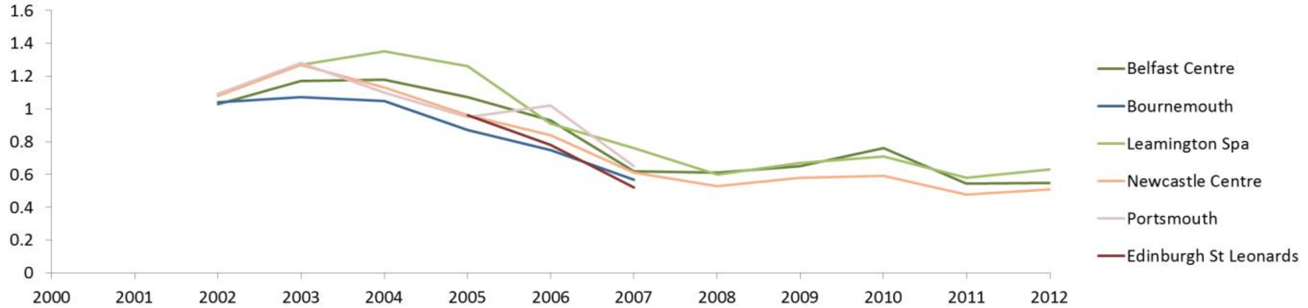


Figure 11 - Long term Non-Automatic benzene annual mean trends.

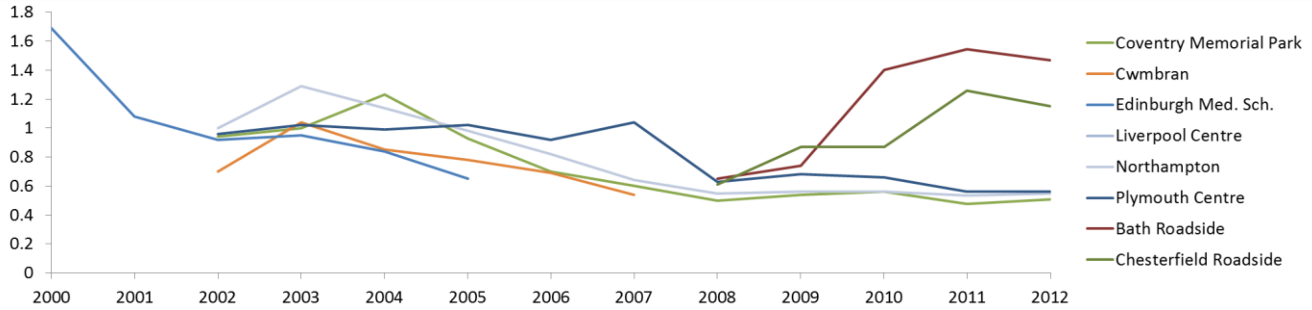


Figure 12 - Long term Non-Automatic benzene annual mean trends.

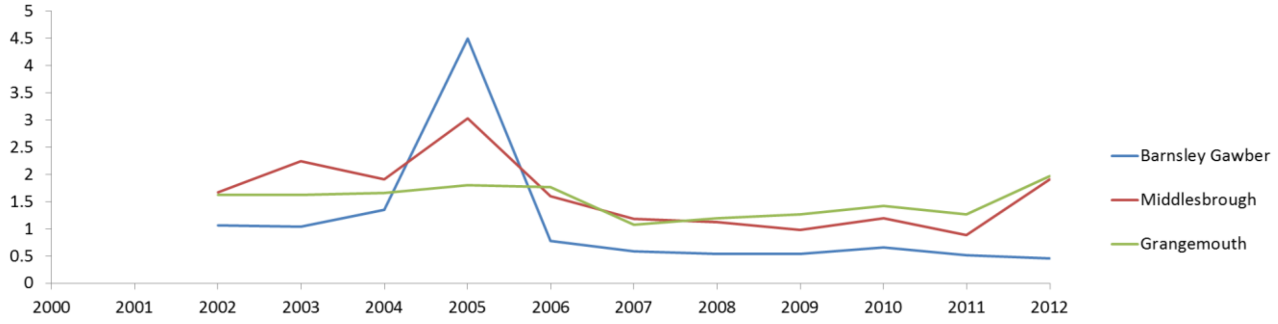


Figure 13 - Bath Roadside long term fortnightly measurements vs AURN NO_x

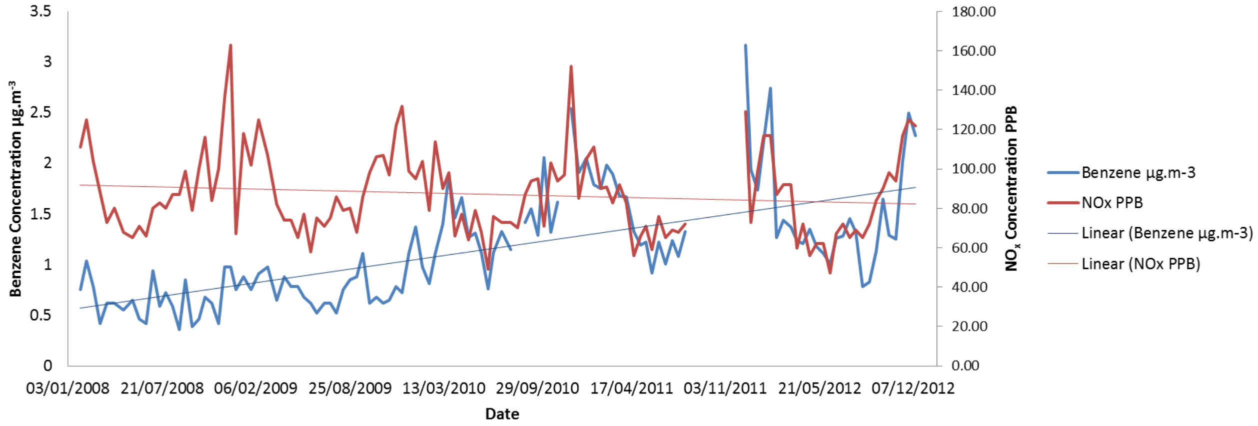


Figure 14 - Chesterfield Roadside long term fortnightly measurements vs AURN NO_x

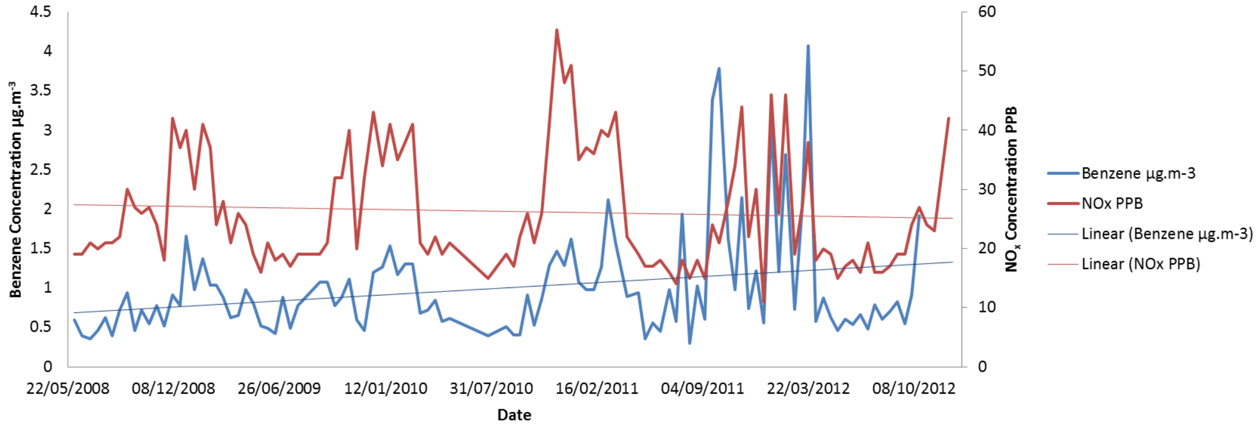
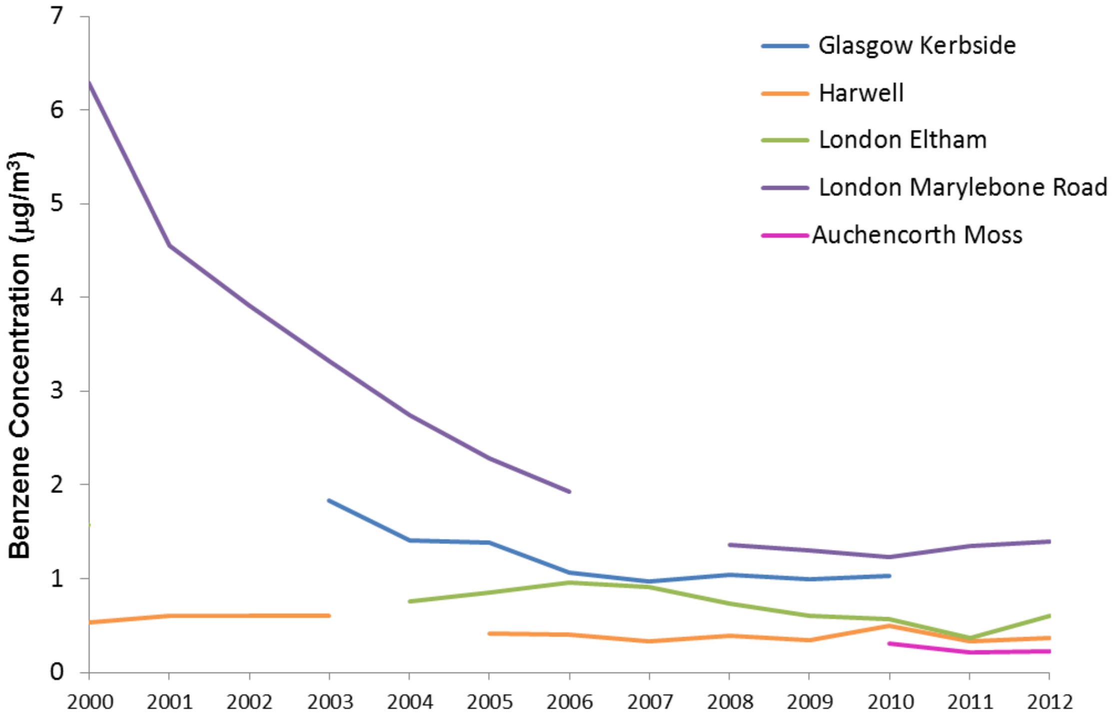


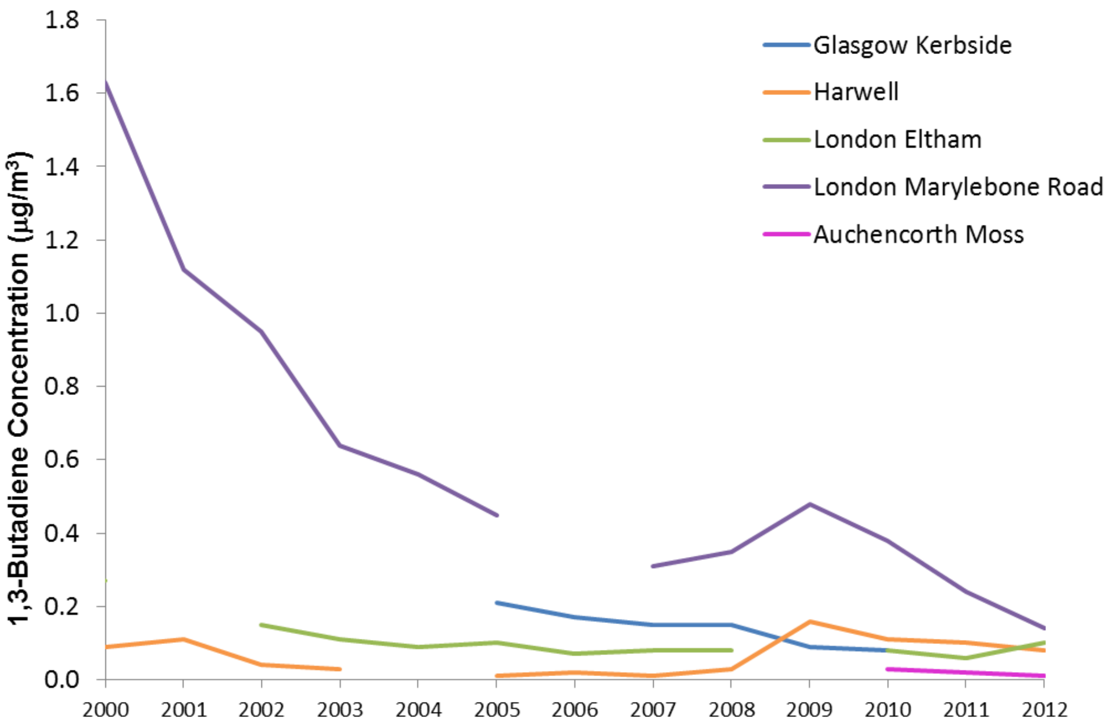
Figure 15 and 16 show the long-term trends of the annual mean concentrations of benzene and 1,3-butadiene at the four sites with long running datasets within the Automatic Hydrocarbon Network, and Auchencorth Moss. Note that in 2010 and 2011 annual mean benzene concentrations have been included for sites where data capture was less than 75%. In other years no data are available where the data capture in the year was less than 75%.

Figure 15 Long term automatic annual mean benzene trends



Note that in 2010 and 2011 annual mean 1,3 butadiene concentrations have been included for sites where data capture was less than 75%. In other years no data are available where the data capture in the year was less than 75%.

Figure 16 Long term automatic annual mean 1,3-butadiene trends



4 Data Quality

4.1 Intercomparisons

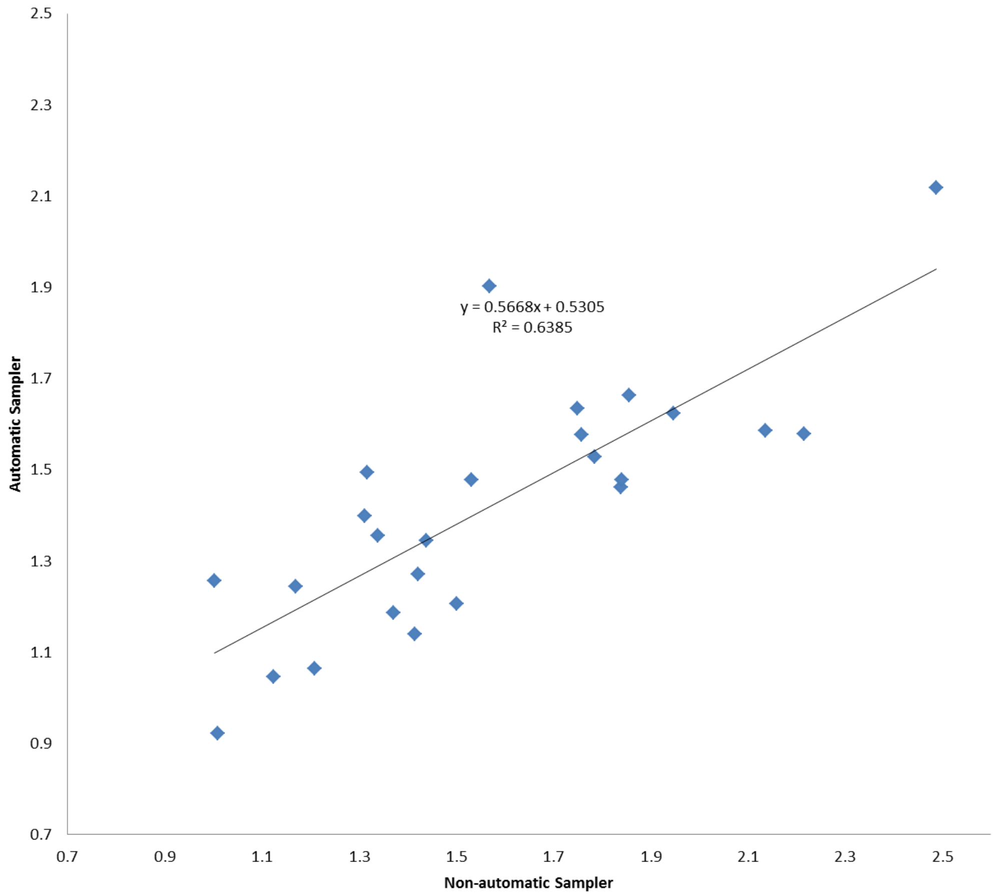
There were two sites at which Non-Automatic samplers and Automatic analysers were collocated; at Marylebone Road, between 14th December 2011 and 21st January 2013 and at London Eltham between 26th April 2011 and 5th July 2012. Comparing data from collocated samplers is a good way to validate the data and can help identify issues such as co-elution of butanol from the Condensation Particle Counter (CPC) at Marylebone Road which can affect the automated benzene measurements. Comparisons from these two sites are shown below.

4.1.1 Marylebone Road

Data is available from the two collocated samplers at Marylebone Road in 2012.

Figure 15 and Figure 16 show x,y scatter plots (only where data capture >75% for both methods). These automatic fortnightly means correspond to the dates of sampling with the non-automatic benzene samplers, so the data may be directly compared.

Figure 17 Comparison of collocated samplers at Marylebone Road 14/12/11-21/01/13

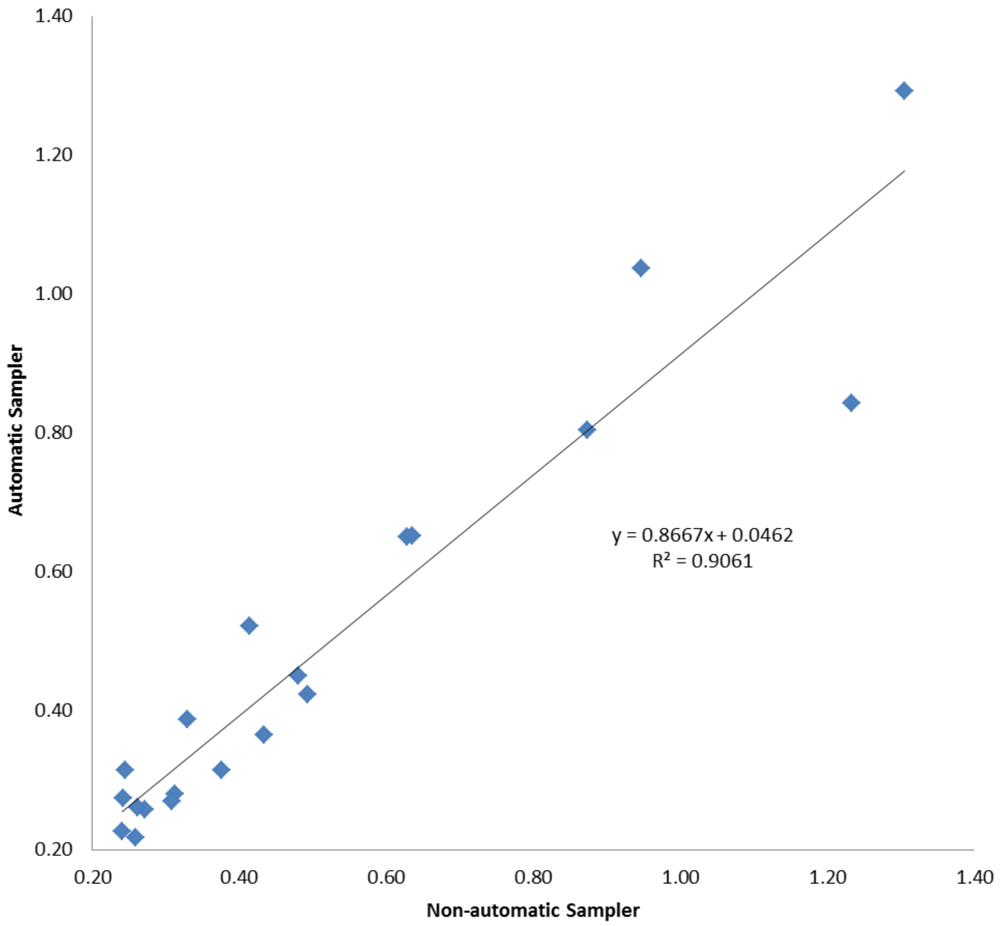


There were 26 measurements when both sampling methods achieved >75% data capture at Marylebone Road (1 outlier was removed). The agreement between the two sites is reasonable but not as close as that shown at Eltham, it is likely that coelution of butanol causes this issue at Marylebone Road, Eltham is not exposed to emissions of butanol.

4.1.2 London Eltham

Data from the collocated samplers at London Eltham have been compared in a similar way and are presented in Figure 16.

Figure 18 Comparison of collocated samplers at London Eltham 26/04/11-05/07/12



There were 22 samples when data capture exceeded 75%, two of these were outliers and were removed. The regression (R^2) of 0.91 at Eltham (Figure 16) shows a better agreement than 0.64 at Marylebone Road (Figure 15).

It seems likely that co-elution of butanol emitted from the Condensation Particle Counter at Marylebone Road affects benzene measurements from the automatic analyser which is in turn affecting the correlation at Marylebone Road.

4.2 Estimation of Uncertainty

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2012 for benzene is 15%, expressed at a 95% level of confidence. This includes contributions from Ricardo-AEA's flow measurements, desorption efficiency and analysis uncertainty.

The requirement for benzene measurement uncertainty from an automatic hydrocarbon analyser is 25%, expressed at 95% confidence limit. The Perkin-Elmer analyser used in the UK network has not been type tested, so an estimate of the various contributions has been made to assess compliance with the DQO requirement. The main contributions are:

- Repeatability and lack of fit – derived if possible from the manufacturers specifications
- Variation in sample gas pressures , surrounding temperature and electrical voltage – derived if possible from the manufacturers specifications

- Interference from ozone – derived if possible from the manufacturers specifications
- Memory effects – derived if possible from the manufacturers specifications
- Differences between the sample and calibration port – these differences are negligible, the sample and calibration port are in contact with 90% of the same valve. Removing the calibration cylinder to evaluate this will disturb the system and affect sample measurements for some considerable time afterwards.
- Uncertainty in calibration gas – from NPL cylinder certificate
- Reproducibility under field conditions – this could be estimated from the manufacturers specifications
- Long term drift – corrections are made such that this is not applicable to the expanded uncertainty.

By far the largest components in the uncertainty budget are lack of fit and calibration gas uncertainty. In the absence of data from type testing, the maximum permissible values stated in the EN Standard have been used. Using these values and the known values from the calibration cylinder the uncertainty budget has been calculated. The uncertainty of benzene measurements using a Perkin-Elmer analyser is estimated to be less than 24%.

Reliability and intercomparability of UK benzene measurements is regularly assessed through international intercomparisons. (Quote the last ACTRIS result Harwell +6.5%, AM -7.6% from reference value). R-AEA will be attending the next intercomparison at JRC in November 2013.

The Standard Method for measurement of benzene with an automatic analyser is in the process of review by CEN Working Group 12.

4.3 Standard Methods

European Standard EN14662-3:2005 is the Ambient Air Quality Standard method for the measurements of benzene concentrations – Part 3: Automated pumped sampling with in-situ gas chromatography. This Standard is for the determination of benzene in ambient air for the purpose of comparing measurement results with annual mean limit values. It describes guidelines for measurements with automated gas chromatographs, between 0 and 50 µg/m^3. Measurements undertaken by the Automatic Hydrocarbon Network are carried out in accordance with this Standard.

European Standard EN14662-1:2005 is the Ambient Air Quality Standard method for measurement of benzene concentrations – Part 1: Pumped sampling followed by thermal desorption and gas chromatography. This Standard gives general guidance for the sampling and analysis of benzene in air by pumped sampling, thermal desorption and capillary gas chromatography. The pumped sampler was developed by NPL in compliance with this standard. Ricardo-AEA contract Environmental Scientifics Groups (ESG) to analyse the samples in accordance with this standard.

There is no standard method for aldehyde measurements. The system used has been constructed broadly in-line with the benzene method in EN14662-1:2005 and using the relevant analysis method suggested by the DNPH tube manufacturers (Waters Inc.)[9]. This method follows the guidance of the EMEP manual for aldehyde measurements[10]. The flow rate and sample time have been adjusted to achieve a volume within the upper and lower limit of the DNPH tube limits as specified by the manufacturer.

[9] Sep-Pak XPoSure Aldehyde Sampler Care and Use manual http://www.waters.com/webassets/cms/support/docs/wat047204.pdf
[10] Nilu, 2001. EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe EMEP manual for sampling and chemical analysis

4.4 Limit of Detection

The Limit of Detection for the mass of benzene on a desorption tube from the Non-Automatic Hydrocarbon Network is approximately 2ng. This is equivalent to about 0.02 µg/m^{3}from a 14 day sample period.

The Limit of Detection for each species measured by the Perkin Elmer Ozone Precursor Analysers used by the Automatic Hydrocarbon Network is shown in Table 8.

Table 8 Automatic Analyser Limits of Detection

Compound	Limit of Detection (µg/m^3)	Compound	Limit of Detection (µg/m^3)
Ethane	0.10	2-Methylpentane	0.04
Ethene	0.01	Isoprene	0.03
Propane	0.02	n-Hexane	0.04
Propene	0.02	Benzene	0.03
Ethyne	0.01	i-Octane	0.05
i-Butane	0.02	n-Heptane	0.04
n-Butane	0.02	n-Octane	0.05
trans-2-Butene	0.02	Toluene	0.04
1-Butene	0.02	Ethylbenzene	0.04
cis-2-Butene	0.02	(m+p)-Xylene	0.04
i-Pentane	0.03	o-Xylene	0.04
n-Pentane	0.03	1,3,5-Trimethylbenzene	0.05
1,3-Butadiene	0.02	1,2,4-Trimethylbenzene	0.05
trans-2-Pentene	0.03	1,2,3-Trimethylbenzene	0.05
1-Pentene	0.03		

5 Developments and Recommendations

5.1 EN14662-3:2005

European Standard EN14662-3:2005 is currently under review by Working Group 12, to bring it in line with the other gaseous pollutants' standards. R-AEA are involved in the review through a representative on the Working Group, and are providing appropriate contributions and feedback to Defra and the Devolved Administrations regarding the potential implications for the Automatic Hydrocarbon Network.

5.2 Acetaldehyde and Formaldehyde

In 2011 the UK Air Quality Expert Group (AQEG) published an advice note on road transport biofuels and their impact on UK air quality for Defra and the Devolved Administrations. The AQEG note can be found at

http://uk-air.defra.gov.uk/documents/110322_AQEG_Biofuels_advice_note.pdf

The note accepts that results from research studies on the effects of biofuels on vehicle emission are inconclusive and show a high degree of variability, but concludes that any increased use of bioethanol and biodiesel are likely to significantly increase acetaldehyde and formaldehyde emissions. The note goes on to say that 'the likely continued growth in biofuel consumption in the UK means that evidence for any atmospheric change in pollutant concentrations should be monitored in parallel with direct measurements of biofuel emissions from road vehicles'.

Starting in 2012, R-AEA started a pilot study monitoring for acetaldehyde and formaldehyde at a small number of roadside and background sites. This will help the UK to prepare for potential legislative change in the future and will start a dataset useful for long term trend analysis.

Use of biofuels in the UK

Biodiesel is a generic term for a product which has variable chemical composition, whereas bioethanol is a specific chemical. Over the past 2-3 years bioethanol and biodiesel consumption has grown, driven by domestic targets and EU Directives. The UK still uses relatively small amounts of low strength bioethanol and biodiesel, but consumption is expected to continue to increase over the next decade as a result of the EU Directive 2009/28/EC which raised the target set for the share of biofuels as a % of energy content by 2020 to 10%.

Most bioethanol in the UK is likely to be consumed as weak (<5%) blends in fossil fuel petrol sold at regular filling stations. Research by Ricardo-AEA, undertaken for the Department for Transport in 2011, indicated that in 2008 176 ktonnes of bioethanol were used in road transport. In 2009 361 ktonnes were used (compared to over 900 ktonnes of biodiesel used each year). Data from HM Revenue and Customs, used for the National Atmospheric Emissions Inventory (NAEI), indicate that bioethanol consumption in the UK was about 3% of total petrol consumption in 2010.

Currently 100% of the UK fleet of passenger cars and light commercial vehicles (both new and older models) can use low ethanol blends, up to 5%. Only 84% of the current fleet can run on 10% bioethanol and less than 1% of the fleet can operate with a high 85% bioethanol/petrol blend. The uptake of high concentration blends of bioethanol (E85) may increase in future if the fuel supply infrastructure develops and the population of vehicles capable of running on this fuel increases.

Bioethanol is mainly added to petrol at refineries and main fuel distribution centres so there is unlikely to be any regional consumption hot spot, rather it is used by all petrol vehicles without motorists being aware. High strength bioethanol (E85) is a niche fuel which can only be used by petrol vehicles that have undergone a conversion, engine re-tuning or flexi-fuelled vehicles able to run on regular unleaded or E85. There may be some dedicated fleets using this fuel in some areas, but these are not believed to be common in the UK.

Effect of bioethanol on acetaldehyde and formaldehyde

The Air Quality Expert Group's report on Road Transport Biofuels (2011) suggests that overall, low strength blends of bioethanol reduce or have little effect on emissions of air quality pollutants. But, even at low strength blends of bioethanol, literature studies show that consumption of bioethanol leads to the significant increase in acetaldehyde and formaldehyde emissions from vehicles compared to petrol consumption. Other VOCs may be increased if a high proportion of bioethanol is used due to its effect on increasing fuel volatility.

Geography of bioethanol consumption

In the UK, consumption is likely to be well dispersed across the country, with no particular hot spots. This is likely to continue, although there may be localised use of some biofuels by captive fleets in areas close to where they are produced, but it is unlikely that consumption would be high enough to observe any changes in ambient concentrations. Currently there is very limited information relating to UK airborne aldehyde emissions. This study will provide us with the basis to monitor aldehyde trends over time such that comparisons can be made when transport fuels contain higher quantities of biofuel in the future.

The UK NAEI uses HM Revenue and Customs (HMRC) national statistics on the consumption of biofuels in the UK. The HMRC produces monthly national statistics on the volume of bioethanol and biodiesel released for consumption. However, this information does not split the bioethanol consumption by region. For the report, '*Improving the Greenhouse Gas Inventories for Road Transport in Scotland, Wales and Northern Ireland*' (Murrells et al. 2011), Devolved Administration contacts and biofuel experts within AEA were consulted regarding data on regional biofuel consumption; however, this information does not seem to be available. Information on the location of the major biofuel producers in the UK is available, however, this does not necessarily represent where the biofuels are consumed. Any variation will also only be a matter of whether the fuel sold is a 0% blend (no bioethanol in petrol) or 5% bioethanol blend and any differences between filling stations in this respect are likely to be random, not with any regional bias. Most large scale biofuel production is used to produce 5% biofuel blends which are expected to be sold uniformly around the UK.

Selection of monitoring sites

The likely continued growth in biofuel consumption in the UK means that evidence for any atmospheric changes in pollutant concentrations should be monitored in parallel with estimates of biofuel emissions from road vehicles. The pilot monitoring project delivers this and monitors the roadside effect of bioethanol use within the UK fleet.

Given that the pattern of consumption of bioethanol relative to petrol consumption is likely to be quite uniform, the strongest signature for ambient concentrations of acetaldehyde and formaldehyde derived from bioethanol consumption will be where petrol vehicle emissions are highest. The places where these emissions will be relatively high will be at roads where:

- The traffic flow is high
- There is a high proportion of petrol car activity – this would favour an urban roadside site rather than a rural or motorway site where there is generally more diesel activity

- The petrol car fleet is relatively old, hence there will be a higher proportion of older Euro standards with higher VOC emissions
- The traffic flow is slow and congested. This enhances vehicle emissions of VOCs.

The following indicators have therefore been used to select the monitoring sites to be used for the study:

- The type of road the monitoring station is located by
- Traffic flow per day
- Proportion of diesel and petrol vehicles which drive by the monitoring site (since the focus of this study is only bioethanol).

To ensure that the results of the monitoring showed the difference in bioethanol consumption specifically, it is also important that the roadside monitoring sites are located at similar heights and are similar distances away from the road.

Ricardo-AEA's work using Automatic Number Plate Recognition (ANPR) data for the NAEI confirmed the mix of petrol cars is highest on urban roads. Previous work analysing ANPR and licensing data suggested the age of the car fleet on the same type of road was fairly uniform in the UK, but there were certain areas of the country which had a consistently older car fleet registered. One of these was the south-west of England.

Acetaldehyde and formaldehyde are types of VOCs that are formed in the atmosphere from the photochemical degradation of other VOCs. In fact, the majority of these aldehydes detected at a given location will be from this secondary background source rather than direct emissions. It will therefore be important to do paired measurements at a reasonably close background site to determine the photochemically produced background. This background concentration will vary by region around the UK and be strongest during photochemically active periods in the spring and summer, but there should be little difference between an urban roadside and urban background site in the same region (e.g. county). The difference (delta) between the two measurements will be a measure of the direct traffic emissions. The delta will vary with time of day and time of year and should be strongest when there is least photochemical activity (e.g. during the winter). The delta should increase over the campaign if the national bioethanol consumption increases by increasing the strength of bioethanol/petrol mix.

Two paired sites are used:

- Chesterfield urban roadside and Chesterfield urban background.
- Exeter roadside and Honiton urban background

The Honiton and Exeter sites should be sufficiently close to have the same photochemical background contribution. The Exeter roadside site is also in an area where the petrol car fleet is known to be slightly older than the national average.

A fifth location is recommended at the rural Yarner Wood (Devon) site. This will provide further evidence on the photochemical background and its seasonal variation and would be a useful indicator of this contribution in its own right for regional scale photochemical air pollution modelling.

Appendices

Appendix 1 – 2012 Audit schedule

Table 9 Non automatic sample flow audits

Site	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min
Barnsley Gawber	18/04/2012	9.88	10	31/10/2012	N/A	10.04	02/04/2013	9.47	9.75
Bath Roadside	28/03/2012	10.12	10	03/10/2012	10.46	9.97	24/04/2013	9.47	10.14
Belfast Centre	27/04/2012	9.29	10.03	18/10/2012	10.39	10.06	17/04/2013	9.73	10.14
Birmingham Acocks Green	23/04/2012	9.39	9.99	10/10/2012	9.96	9.98	11/04/2013	10.61	9.97
Birmingham Tyburn Roadside	04/04/2012	10.15	10.05	10/10/2012	8.99	10.01	11/04/2013	10.27	10.07
Bristol Old Market	23/04/2012	10.77	10.04	03/10/2012	9.62	-	-	-	-
Bury Roadside	19/04/2012	9.88	10.01	13/11/2012	9.82	9.97	03/04/2013	9.61	9.86
Cambridge Roadside	16/04/2012	9.69	10	17/10/2012	10.49	9.96	08/04/2013	9.43	10.00
Camden Kerbside	24/04/2012	9.88	9.91	23/10/2012	9.74	10.09	16/04/2013	9.57	10.03
Carlisle Roadside	03/04/2012	9.63	9.95	03/10/2012	10.19	9.99	08/04/2013	9.59	10.02
Chatham Roadside	13/03/2012	9.36	10.01	15/10/2012	10.67	10.01	04/04/2013	8.57	10.09
Chesterfield Roadside	17/04/2012	9.54	10.01	31/10/2012	10.20	9.94	22/04/2013	10.82	10.07
Coventry Memorial Park	23/04/2012	10.39	10.01	11/10/2012	9.85	10.17	-	-	-
Glasgow Kerbside	02/05/2012	8.7	10	08/10/2012	7.08	9.85	15/04/2013	10.08	9.99
Grangemouth	04/04/2012	8.55	10.06	08/10/2012	10.43	10.02	15/04/2013	10.64	10.00
Haringey Roadside	26/04/2012	9.88	9.96	22/10/2012	9.46	9.89	19/04/2013	20.29	10.05
Leamington Spa	19/03/2012	10.13	10.02	12/10/2012	10.48	10.06	18/04/2013	9.39	9.99
Leeds Centre	13/03/2012	9.53	9.78	31/10/2012	10.19	10.04	02/04/2013	10.18	9.98
Leicester Centre	17/04/2012	10.09	10.01	23/10/2012	9.46	9.96	-	-	-
Liverpool Speke	25/04/2012	10.33	10.06	14/11/2012	9.41	9.98	10/04/2013	9.73	9.99
London Bloomsbury	19/04/2012	9.87	9.98	24/10/2012	9.82	10.06	15/04/2013	10.07	9.92

Site	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min
Manchester Piccadilly	19/04/2012	10.51	10.01	11/10/2012	9.95	10.09	04/04/2013	9.59	9.90
Middlesbrough	11/04/2012	9.55	10.02	02/10/2012	10.35	10.00	10/04/2013	9.49	10.00
Newcastle	03/04/2012	9.05	9.97	02/10/2012	10.49	10.12	09/04/2013	9.85	10.02
Newport	-	-	-	31/10/2012	-	10.08	02/04/2013	10.45	9.97
Northampton	19/03/2012	9.55	10.1	24/10/2012	10.08	-	-	-	-
Norwich - Lakenfields	01/05/2012	9.71	9.95	16/10/2012	10.11	10.02	09/04/2013	9.57	10.14
Nottingham Centre	03/04/2012	10.43	10.14	31/10/2012	-	10.04	15/04/2013	9.56	10.08
Oxford Centre Roadside	02/02/2012	10.02	10	25/10/2012	10.27	10.06	23/04/2013	9.83	10.01
Oxford St Ebbes	05/04/2012	9.2	10.03	25/10/2012	10.88	9.99	23/04/2013	9.48	10.06
Plymouth	03/05/2012	9.76	9.9	01/10/2012	9.98	-	-	-	-
Scunthorpe Town	-	-	-	13/11/2012	-	10.00	08/04/2013	9.94	10.07
Sheffield Centre	17/04/2012	9.96	10.01	31/10/2012	9.91	9.99	23/04/2013	9.71	10.01
Southampton	03/04/2012	9.75	9.92	02/10/2012	9.92	10.21	22/04/2013	9.66	10.13
Stockton-on-Tees Eaglescliffe	11/04/2012	9.83	10.04	29/08/2012	10.27	10.03	10/04/2013	9.75	10.00
Stoke-on-Trent Centre	22/03/2012	9.24	9.65	09/10/2012	9.70	10.05	24/04/2013	9.87	10.02
Tower Hamlets Roadside	-	-	-	05/11/2012	-	10.11	18/04/2013	9.86	10.00
Wigan Centre	23/04/2012	9.68	9.98	09/10/2012	9.95	-	-	-	-
York Bootham	-	-	-	06/11/2012	-	10.01	09/04/2013	10.32	10.06
York Fishergate Roadside	16/04/2012	9.64	10.01	30/10/2012	10.26	10.05	09/04/2013	9.82	10.07

2012 Audit Schedule of the Automatic Hydrocarbon Network

Table 10 Audit and service schedule of the automatic hydrocarbon analysers

Site	Service Date	Audit Date	Audit Date	Service Date
Auchencorth Moss	27/10/11	18/05/11	28/03/12	16/01/2013
Harwell	27/06/11	14/03/11	12/04/12	05/09/2013
Eltham	22/11/11	16/03/11	22/03/12	13/09/13
Marylebone Road	15/03/11	15/03/11	20/03/12	09/03/2013

Appendix 2

Data capture, maximum and annual mean values from the Automatic Hydrocarbon Network

Percentage data capture, maximum and annual mean values of ratified data from the Auchencorth Moss site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means, therefore, may not be representative of an average year and the data should be used with caution.

Table 11 Auchencorth Moss statistics, 2012

Compound	% Data capture	Maximum hourly concentration (µg/m^3)	Annual Mean concentration (µg/m^3)
1,2,3-trimethylbenzene	<LOD	<LOD	<LOD
1,2,4-trimethylbenzene	<LOD	<LOD	<LOD
1,3,5-trimethylbenzene	<LOD	<LOD	<LOD
1,3-butadiene	80	0.7	0.022
1-butene	<LOD	<LOD	<LOD
1-pentene	<LOD	<LOD	<LOD
2-methylpentane	83	4.6	0.072
benzene	90	2.8	0.23
ethane	89	16	1.9
ethylbenzene	44	9.2	0.044
ethene	18	1.9	0.070
ethyne	86	2.4	0.14
isoprene	31	1.8	0.085
propane	89	130	1.4
propene	50	1.9	0.035
toluene	84	58	0.19
cis-2-butene	<LOD	<LOD	<LOD
iso-butane	86	23	0.34
iso-octane	26	9.6	0.047
iso-pentane	86	9.8	0.15
m+p-xylene	52	29	0.13
n-butane	77	36	0.41
n-heptane	41	4.4	0.083
n-hexane	85	8.2	0.072
-octane	37	1.7	0.047
n-pentane	88	11	0.090
o-xylene	48	8.8	0.044
trans-2-butene	<LOD	<LOD	<LOD
trans-2-pentene	<LOD	<LOD	<LOD

Percentage data capture, maximum and annual mean values of ratified data from the Harwell site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means, therefore, may not be representative of an average year and the data should be used with caution.

Table 12 Harwell statistics 2012

Compound	% Data capture	Maximum hourly concentration (µg/m^3)	Annual Mean concentration (µg/m^3)
1,2,3-trimethylbenzene	60	0.70	0.10
1,2,4-trimethylbenzene	56	2.8	0.15
1,3,5-trimethylbenzene	22	0.60	0.10
1,3-butadiene	95	1.3	0.09
1-butene	65	1.3	0.09
1-pentene	<LOD	<LOD	<LOD
2-methylpentane	93	6.1	0.11
benzene	93	3.1	0.36
ethane	96	19	2.7
ethylbenzene	48	1.6	0.13
ethene	93	7.3	0.43
ethyne	91	3.0	0.27
isoprene	25	0.59	0.06
propane	95	25	1.5
propene	84	3.0	0.23
toluene	87	16	0.50
cis-2-butene	89	0.16	0.047
iso-butane	94	15	0.48
iso-octane	32	2.4	0.14
iso-pentane	95	6.4	0.39
m+p-xylene	60	6.4	0.26
n-butane	95	27	0.80
n-heptane	48	2.6	0.12
n-hexane	93	2.1	0.11
n-octane	17	0.57	0.09
n-pentane	95	3.4	0.21
o-xylene	51	2.4	0.18
trans-2-butene	95	0.40	0.047
trans-2-pentene	<LOD	<LOD	<LOD

Percentage data capture, maximum and annual mean values of ratified data from the London Eltham site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means, therefore, may not be representative of an average year and the data should be used with caution.

Table 13 London Eltham statistics 2012

Compound	% Data capture	Maximum hourly concentration (µg/m^3)	Annual Mean concentration (µg/m^3)
1,2,3-trimethylbenzene	86	3.3	0.25
1,2,4-trimethylbenzene	50	3.3	0.45
1,3,5-trimethylbenzene	65	1.8	0.15
1,3-butadiene	90	1.4	0.09
1-butene	89	1.4	0.09
1-pentene	87	2.1	0.06
2-methylpentane	91	18	0.43
benzene	89	12	0.62
ethane	86	94	6.1
ethylbenzene	90	5.7	0.26
ethene	83	17	0.79
ethyne	90	4.3	0.35
isoprene	64	7.0	0.23
propane	90	33	2.8
propene	89	4.5	0.37
toluene	89	43	1.2
cis-2-butene	81	0.79	0.05
iso-butane	90	24	1.5
iso-octane	75	7.9	0.19
iso-pentane	90	47	1.7
m+p-xylene	84	18	0.75
n-butane	90	36	2.8
n-heptane	89	4.5	0.17
n-hexane	91	16.3	0.29
n-octane	85	1.6	0.09
n-pentane	91	17	0.81
o-xylene	88	5.9	0.31
trans-2-butene	85	1.0	0.07
trans-2-pentene	87	5.0	0.06

Percentage data capture, maximum and annual mean values of ratified data from the Marylebone Road site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means, therefore, may not be representative of an average year and the data should be used with caution.

Table 14 Marylebone Road statistics 2012

Compound	% Data capture	Maximum hourly concentration (µg/m^3)	Annual Mean concentration (µg/m^3)
1,2,3-trimethylbenzene	90	3.3	0.50
1,2,4-trimethylbenzene	71	9.0	1.0
1,3,5-trimethylbenzene	86	9.4	0.60
1,3-butadiene	88	2.0	0.13
1-butene	73	2.6	0.40
1-pentene	84	1.5	0.15
2-methylpentane	90	20	1.1
benzene	88	7.7	1.4
ethane	91	70	9.5
ethylbenzene	86	7.1	0.93
ethene	90	16	2.7
ethyne	88	11	1.2
isoprene	2	2.2	0.23
propane	90	365	6.0
propene	89	6.1	1.3
toluene	84	64	4.9
cis-2-butene	20	0.93	0.14
iso-butane	90	75	3.3
iso-octane	87	9.5	0.71
iso-pentane	89	48	5.0
m+p-xylene	85	24	3.0
n-butane	90	47	5.3
n-heptane	87	11	0.54
n-hexane	90	8.2	0.68
n-octane	84	5.8	0.19
n-pentane	91	18	2.1
o-xylene	84	7.9	1.2
trans-2-butene	24	1.4	0.14
trans-2-pentene	86	1.9	0.17

Appendix 3

Figure 19 Current non automatic audit certificate

0401

RICARDO-AEA

Certificate of Calibration

Ricardo-AEA,The Gemini Building, Fermi Avenue, Harwell, Didcot, Oxon, OX11 0QR 01235 753000

Certificate Number: 2814

Page 1 of 2

Approved Signatories:	S Eaton B Stacey	D Hector S Stratton
Signed:		
Date of issue:	13 June 2013	
Customer Name and Address:	Dr Daniel Waterman Science and Evidence Team Atmosphere and Local Environment (ALE) Programme Department for Environment, Food and Rural Affairs Area 5E Ergon House, 17 Smith Square, London, SW1P 3JR	
Description:	Measured flow rates for non-automatic benzene samplers in the UK Hydrocarbons Network	

Measured flowrates

Site	Date of measurement	Flow A (mlmin-^{1})	Flow B (mlmin^{-1})	Difference (mlmin^{-1})	Uncertainty (mlmin^{-1})
Barnsley Gawber	02/04/2013	9.75	9.81	0.06	0.003
Bath Roadside	24/04/2013	10.14	10.10	0.04	0.003
Belfast Centre	17/04/2013	10.14	10.10	0.04	0.003
Birmingham Acocks Green	17/04/2013	9.97	10.00	0.03	0.003
Birmingham Tyburn Roadside	11/04/2013	10.07	10.04	0.03	0.003
Bury Roadside	03/04/2013	9.86	9.90	0.04	0.003
Cambridge Roadside	08/04/2013	10.00	10.05	0.06	0.003
Camden Kerbside	16/04/2013	10.03	10.01	0.02	0.002
Carlisle Roadside	17/04/2013	10.02	10.00	0.02	0.002
Chatham Centre Roadside	04/04/2013	10.09	10.10	0.02	0.002
Chesterfield Roadside	22/04/2013	10.07	10.06	0.01	0.002
Glasgow Kerbside	15/04/2013	9.99	10.02	0.03	0.003
Grangemouth	15/04/2013	10.00	10.02	0.02	0.002
Haringey Roadside	19/04/2013	10.05	9.98	0.07	0.003
Leamington Spa	18/04/2013	9.99	10.01	0.02	0.002

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2 providing a level of confidence of approximately 95% The uncertainty evaluation has been carried out in accordance with UKAS requirements.

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

Ricardo-AEA Ltd, A subsidiary of Ricardo Plc.
Registered Office: Shoreham Technical Centre, Shoreham-by-Sea, West Sussex, BN43 5FG, UK
Registered in England and Wales no 8229264

RICARDO-AEA

Certificate Number: 2814

0401

UKAS CALIBRATION

Site	Date of measurement	Flow A (mlmin-^{1})	Flow B (mlmin^{-1})	Difference (mlmin^{-1})	Uncertainty (mlmin^{-1})
Leeds Centre	02/04/2013	9.98	10.02	0.040	0.003
Liverpool Speke	10/04/2013	9.99	10.07	0.084	0.003
London Bloomsbury	15/04/2013	9.92	9.92	0.002	0.002
Tower Hamlets Roadside	18/04/2013	10.00	10.19	0.19	0.005
Manchester Piccadilly	04/04/2013	9.90	9.93	0.029	0.002
Middlesbrough	10/04/2013	10.00	10.00	0.00	0.002
Newcastle Centre	09/04/2013	10.02	10.02	0.00	0.002
Newport	02/04/2013	9.97	9.96	0.01	0.002
Norwich Lakenfields	09/04/2013	10.14	10.07	0.07	0.003
Nottingham Centre	15/04/2013	10.08	10.03	0.05	0.003
Oxford Centre Roadside	23/04/2013	10.01	10.03	0.03	0.002
Oxford St Ebbes	23/04/2013	10.06	9.99	0.07	0.003
Scunthorpe Town	08/04/2013	10.07	10.13	0.07	0.003
Sheffield Centre	23/04/2013	10.01	10.07	0.06	0.003
Southampton Centre	22/04/2013	10.13	10.12	0.02	0.002
Stockton-on-Tees Eaglescliffe	10/04/2013	10.00	10.00	0.00	0.002
Stoke-on-Trent Centre	24/04/2013	10.02	9.99	0.03	0.002
York Bootham	09/04/2013	10.06	10.03	0.04	0.003
York Fishergate	09/04/2013	10.07	10.05	0.02	0.002

The measured flow rate (where this is applicable) is the flow rate through the two sample tubes on the day of audit using documented methods. Flows are corrected to 20°C and 1 atm. . Note that the test results are valid on the day of test only, as flowrate drift over time cannot be quantified.

The reported uncertainty is based on a standard uncertainty multiplied by a coverage factor k = 2 , providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

Appendix 4

Automatic Hourly Mean Graphs for Benzene and 1, 3-Butadiene

Figure 20 Auchencorth Moss 1,3-Butadiene hourly mean concentrations 2012

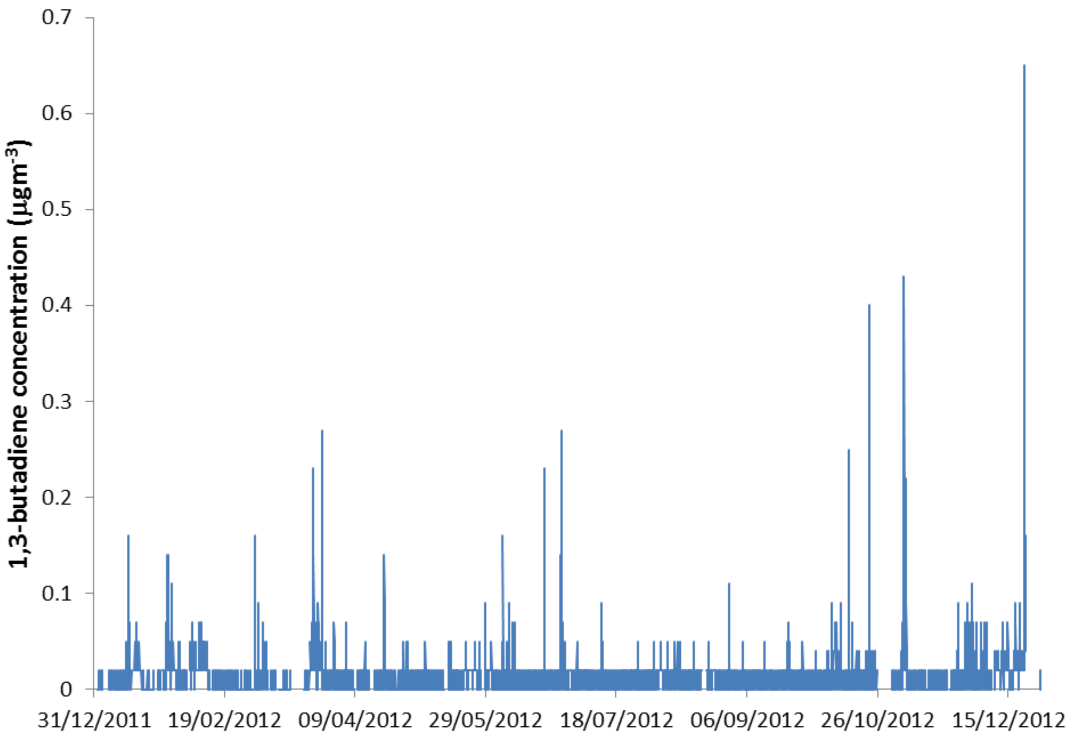


Figure 21 Auchencorth Moss Benzene hourly mean concentrations 2012

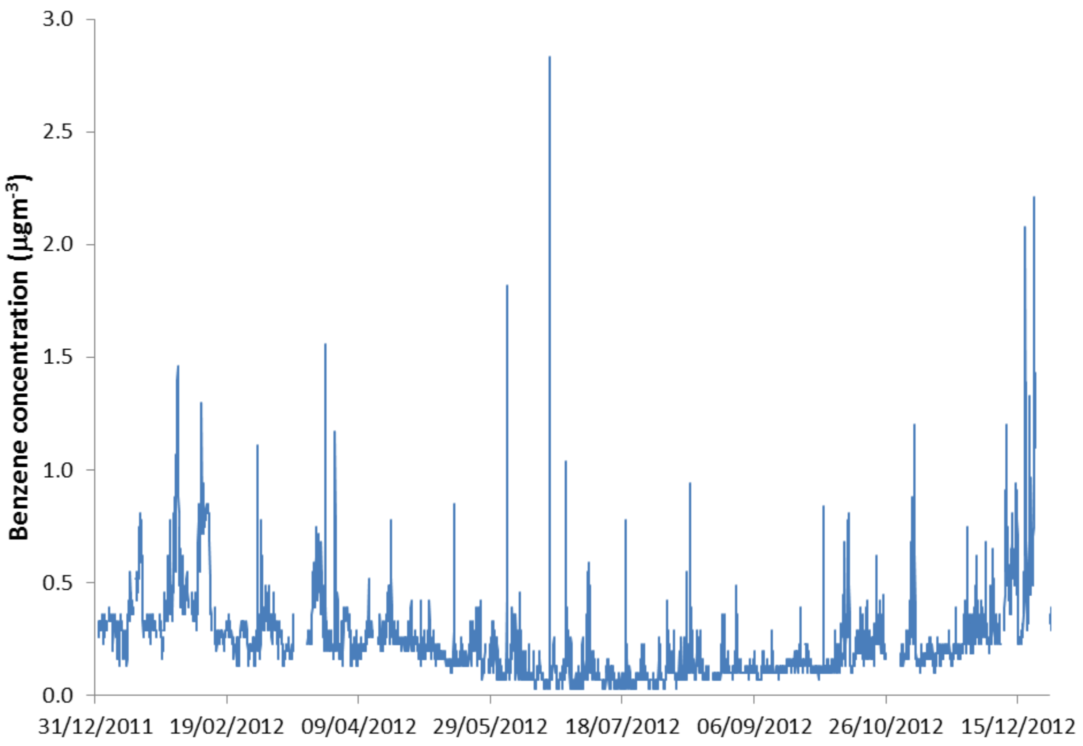


Figure 22   Harwell 1,3-Butadiene hourly mean concentrations 2012

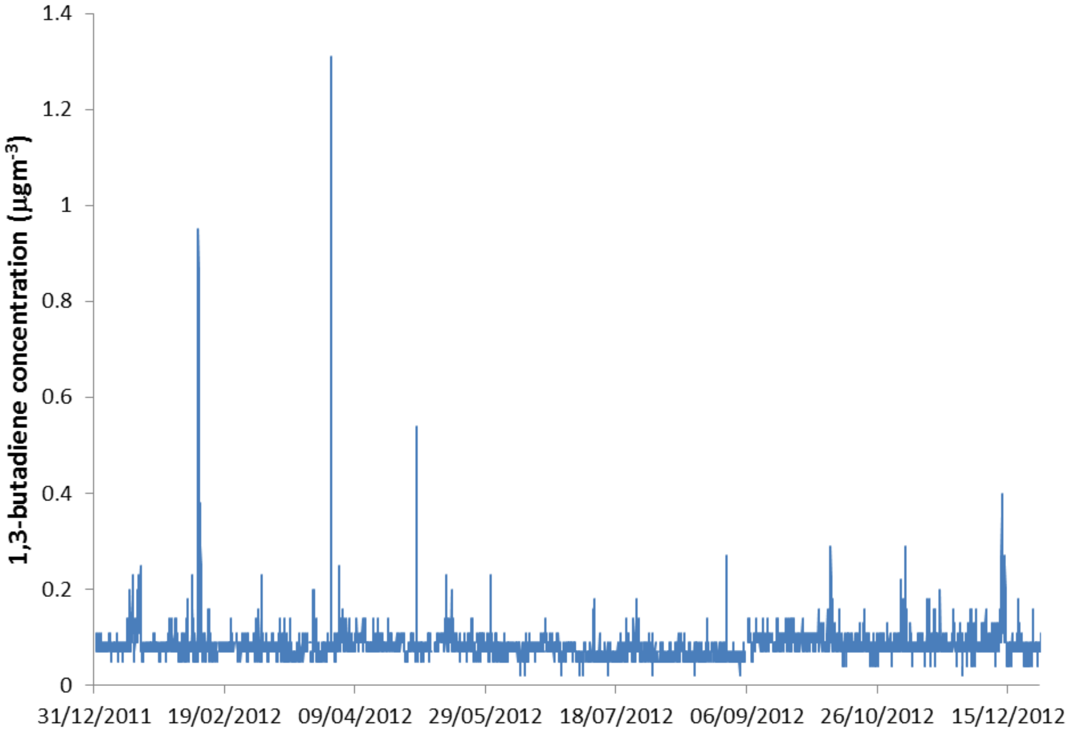


Figure 23   Harwell Benzene hourly mean concentrations 2012

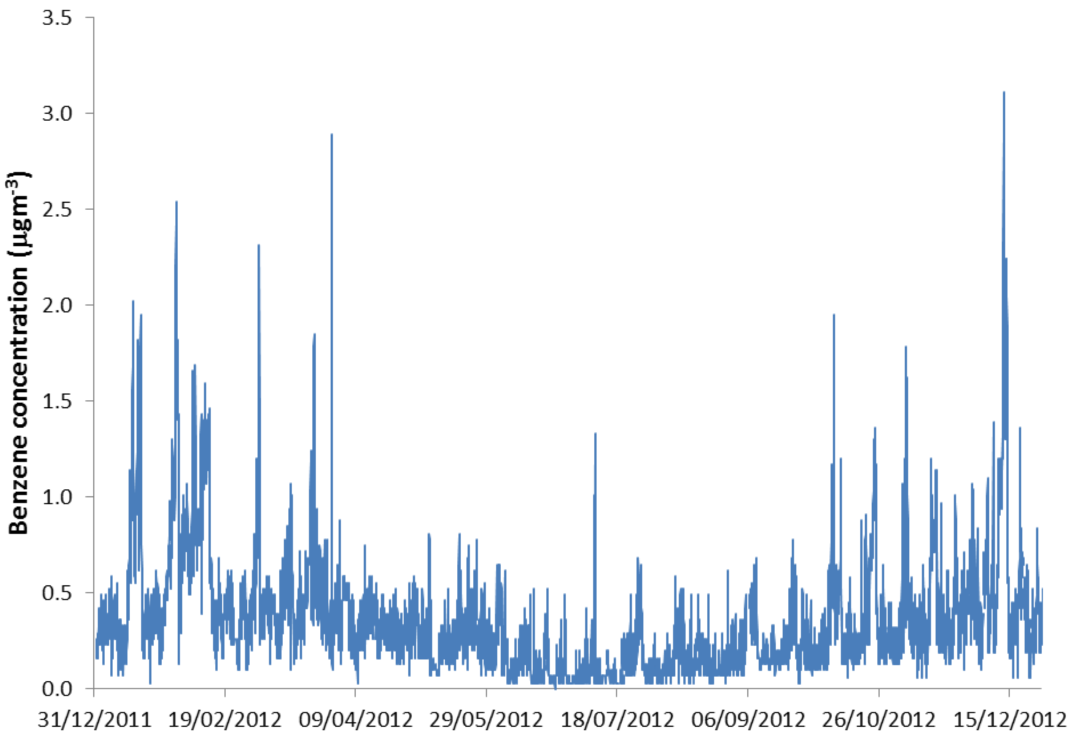


Figure 24 London Eltham 1,3-Butadiene hourly mean concentrations 2012

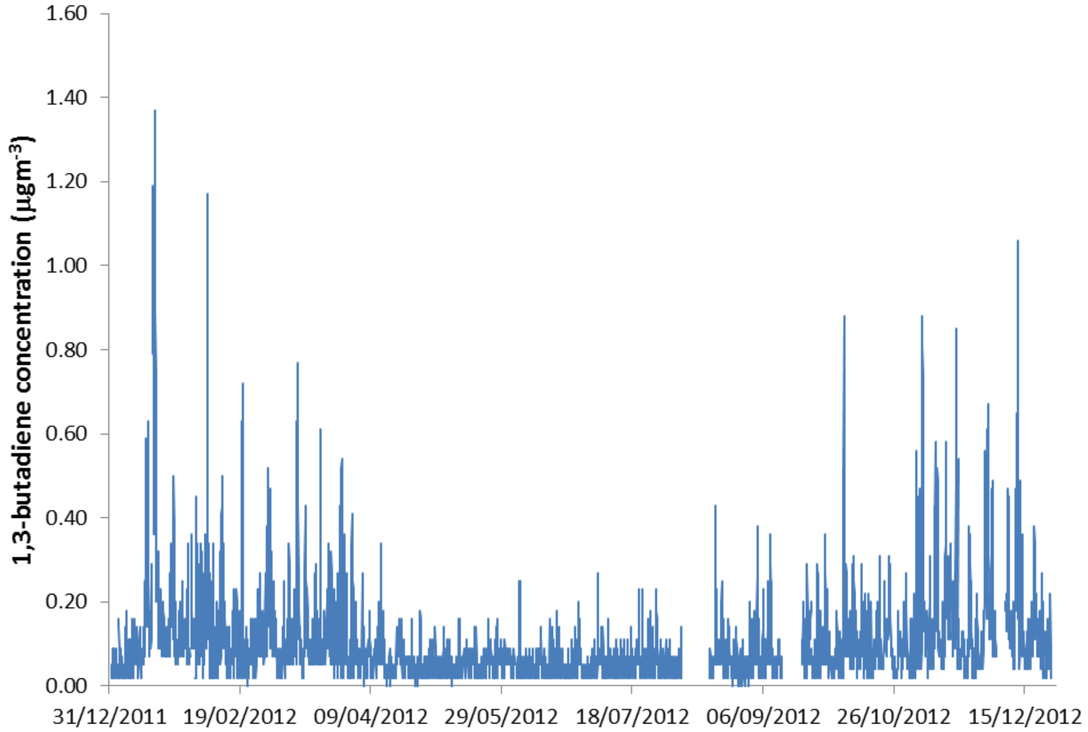


Figure 25 London Eltham Benzene hourly mean concentrations 2012

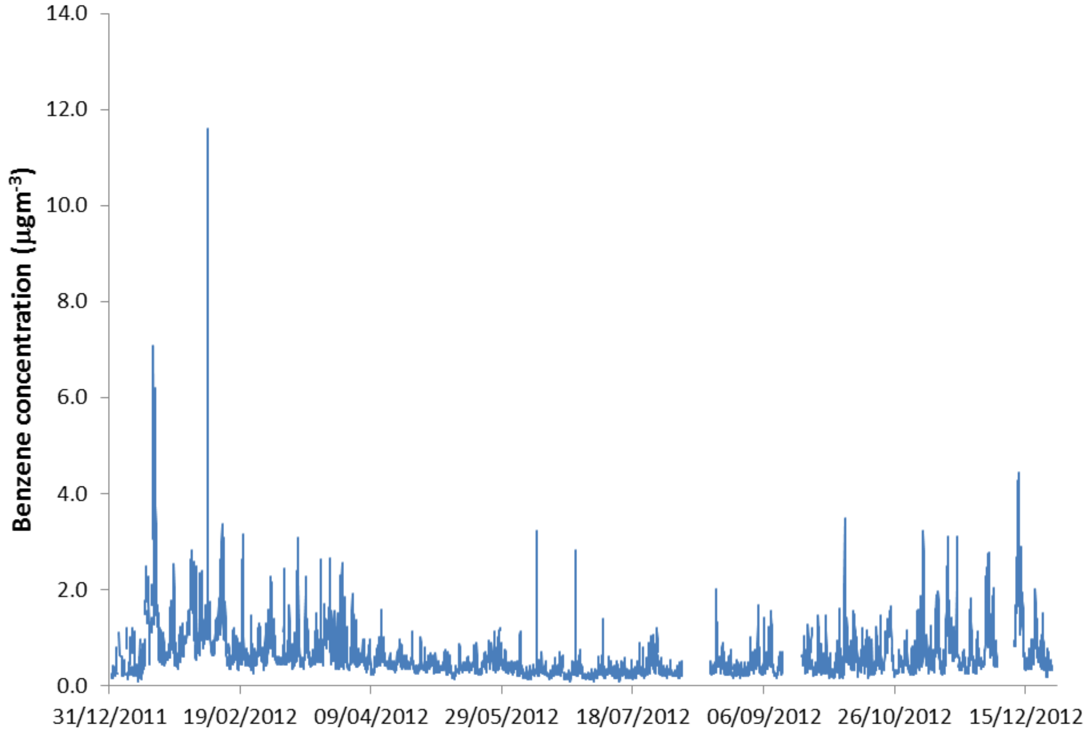


Figure 26 London Marylebone Road 1,3-Butadiene hourly mean concentrations 2012

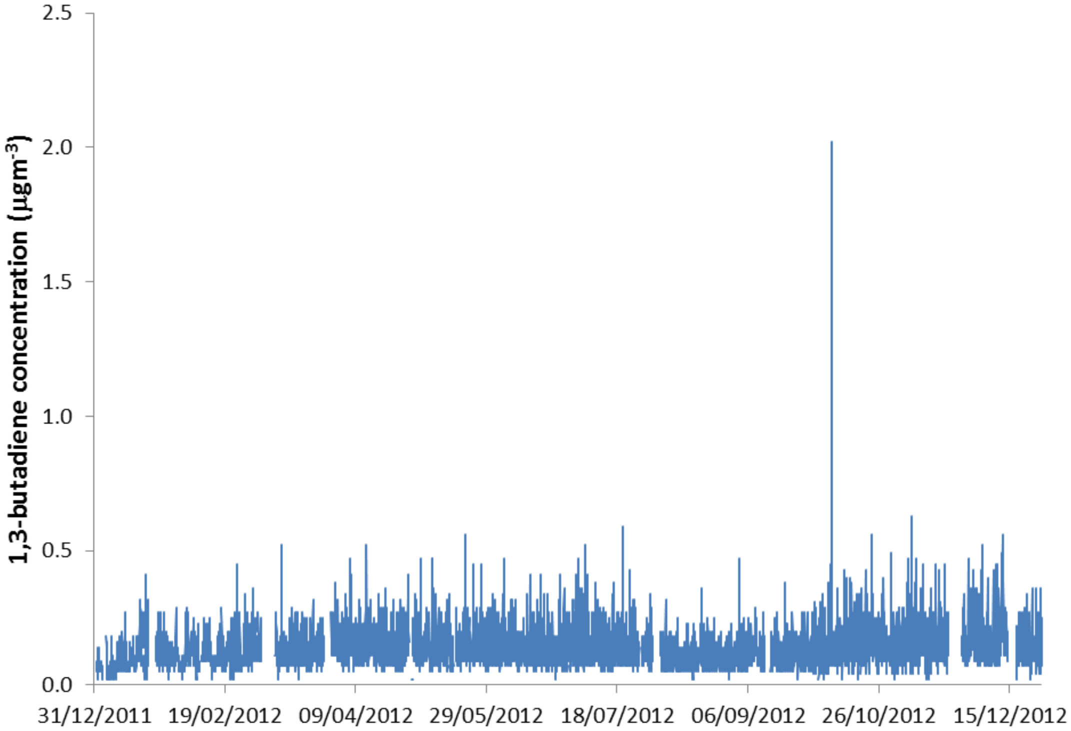
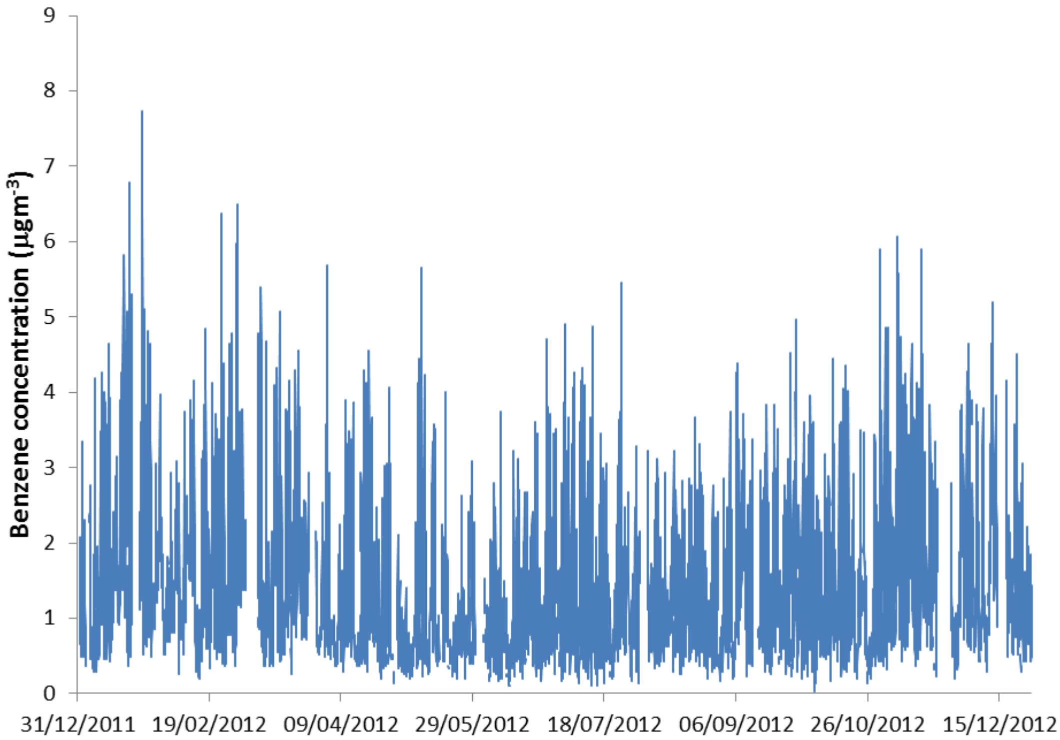


Figure 27 London Marylebone Road Benzene hourly mean concentrations 2012



Non Automatic Fortnightly Mean Graphs for Benzene

Figure 28 Barnsley Gawber Non Automatic fortnightly Benzene

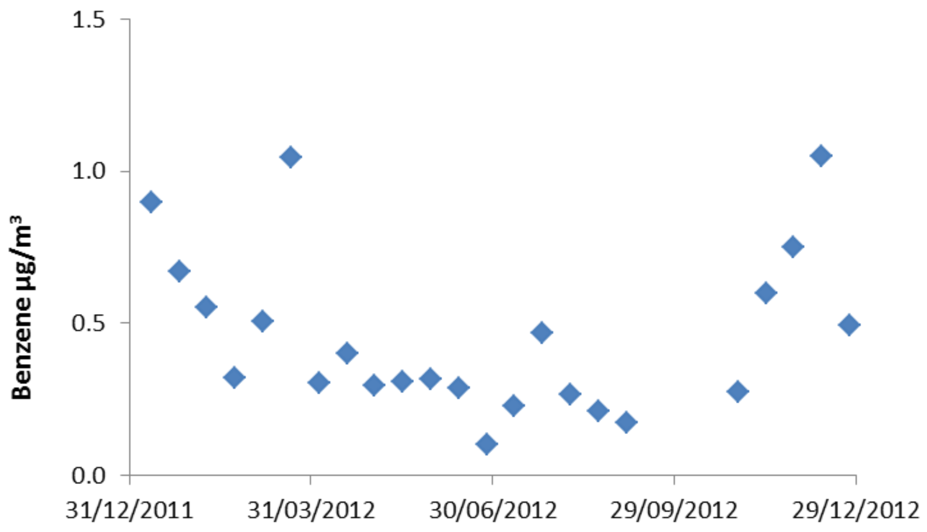


Figure 29 Bath Roadside Non Automatic fortnightly benzene

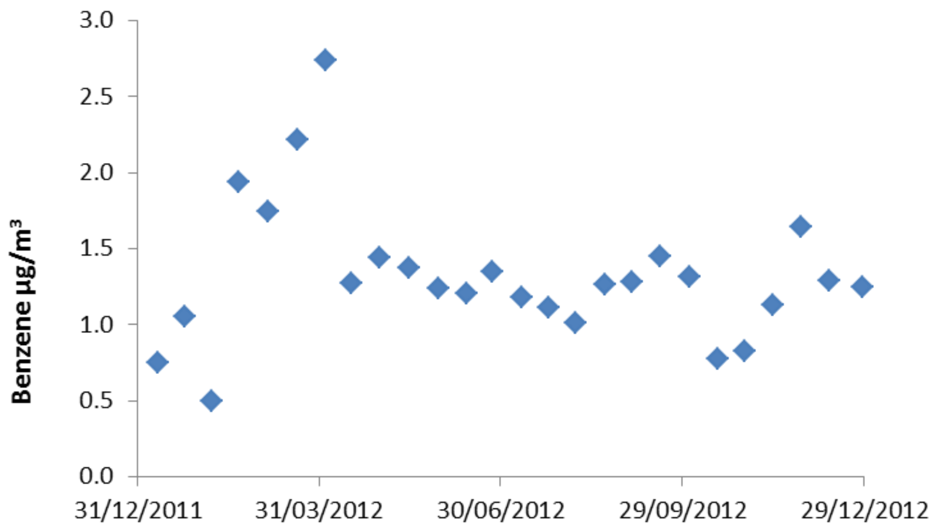


Figure 30 Belfast Centre Non Automatic fortnightly Benzene

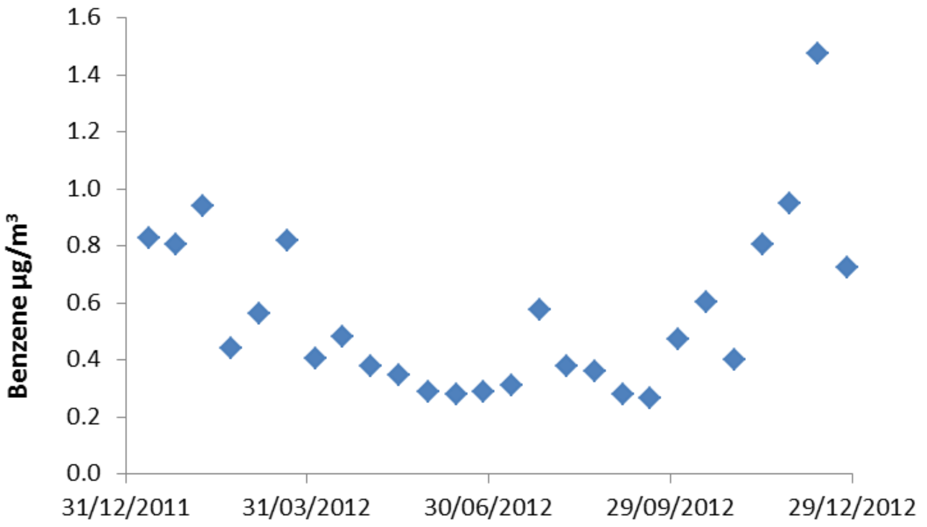


Figure 31 Birmingham Acocks Green Non Automatic fortnightly Benzene

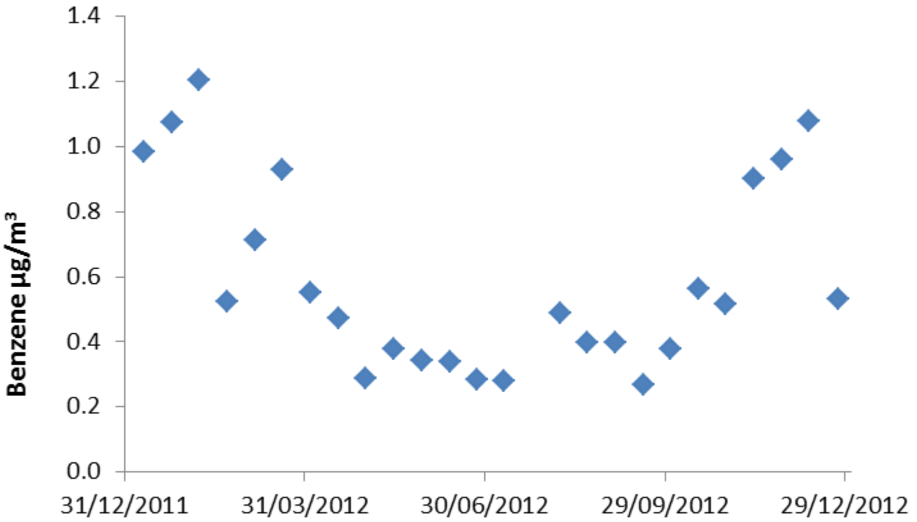


Figure 3230 Birmingham Tyburn Roadside Non Automatic fortnightly Benzene

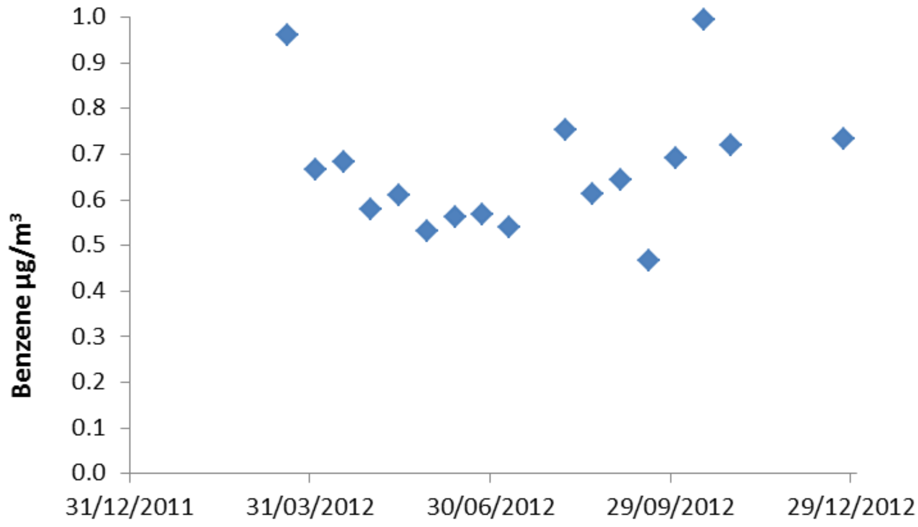


Figure 33 Bristol Old Market Non Automatic fortnightly Benzene

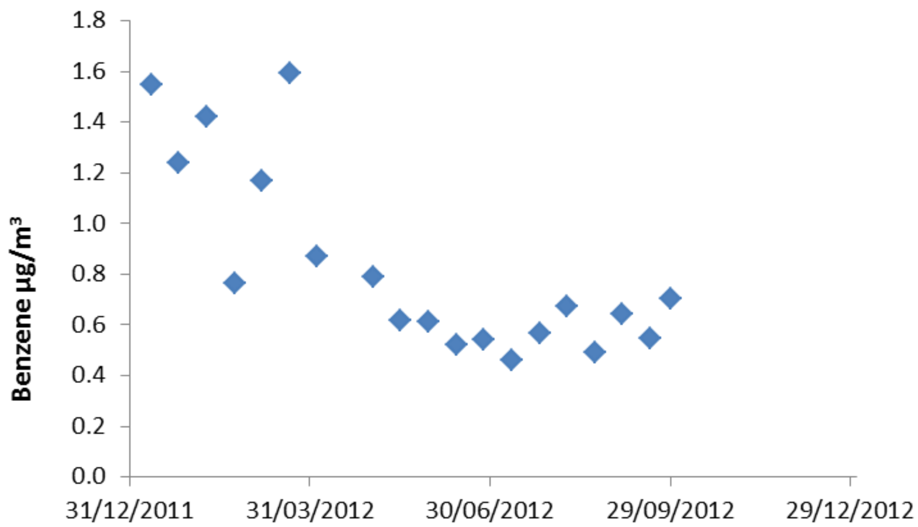


Figure 34   Bury Roadside Non Automatic fortnightly Benzene

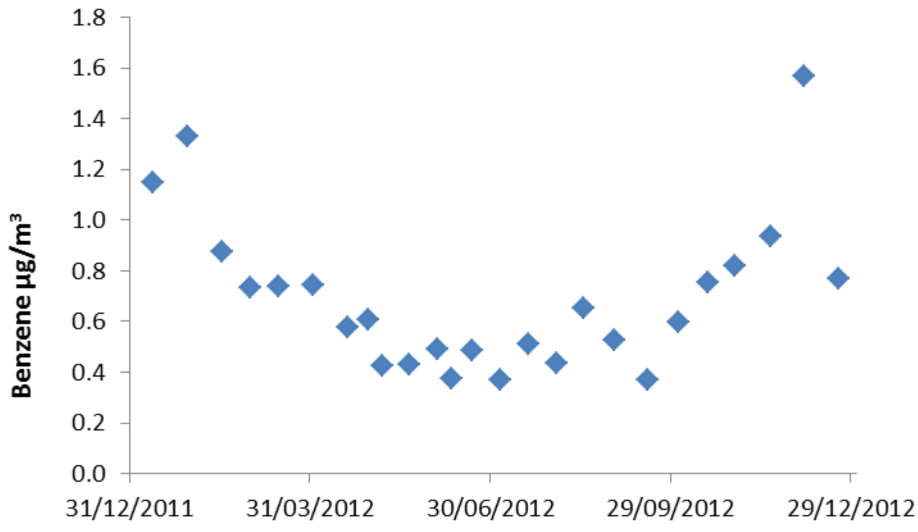


Figure 35   Cambridge Roadside Non Automatic fortnightly Benzene

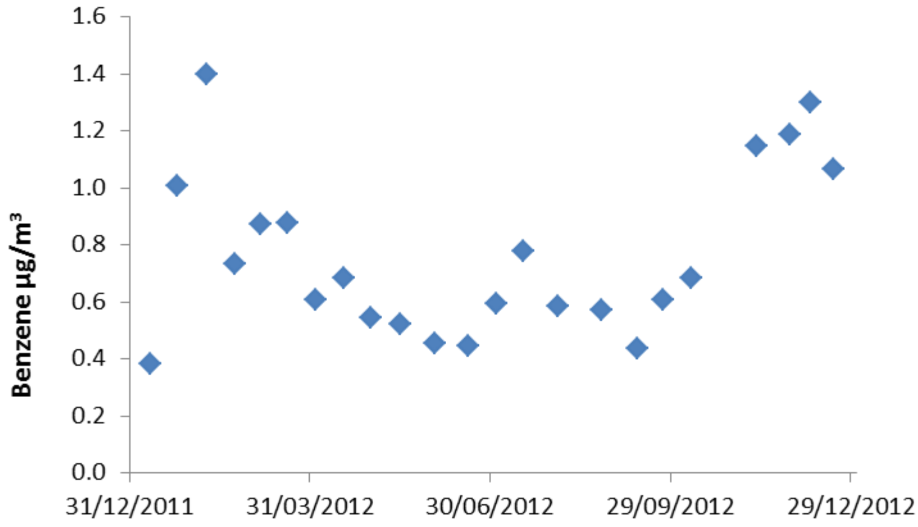


Figure 36 Camden Kerbside Non Automatic fortnightly Benzene

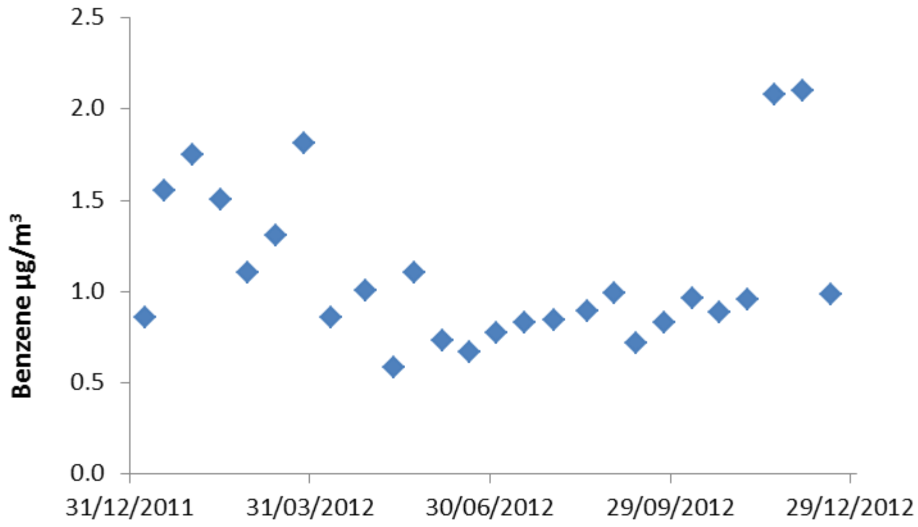


Figure 37 Carlisle Roadside Non Automatic fortnightly Benzene

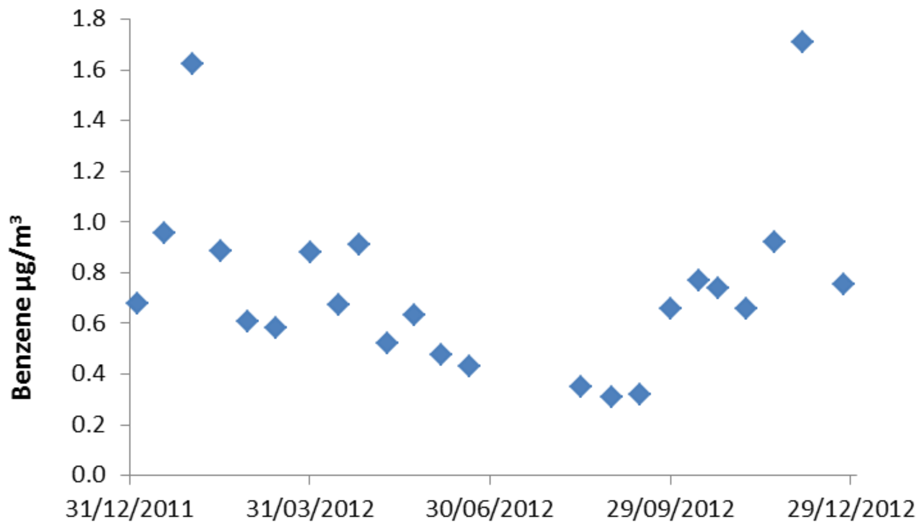


Figure 38   Chatham Roadside Non Automatic fortnightly Benzene

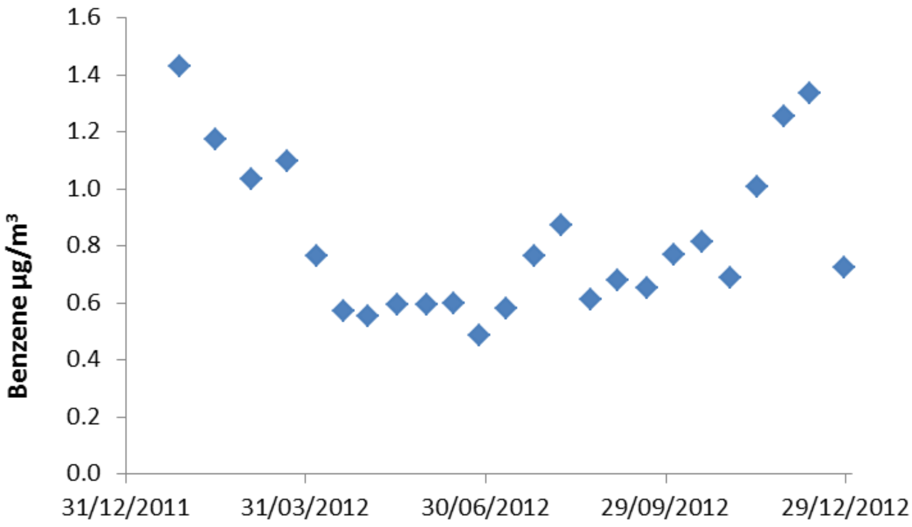


Figure 39   Chesterfield Roadside Non Automatic fortnightly Benzene

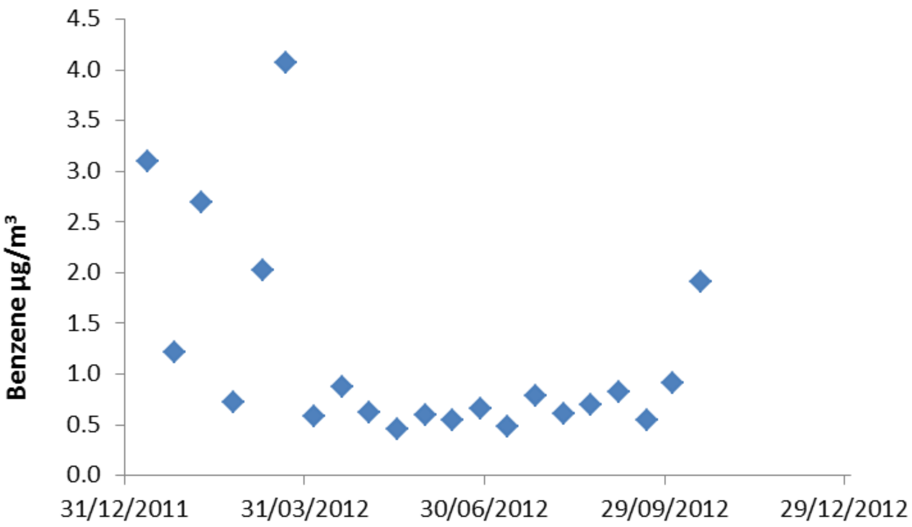


Figure 40 Coventry Memorial Park Non Automatic fortnightly Benzene

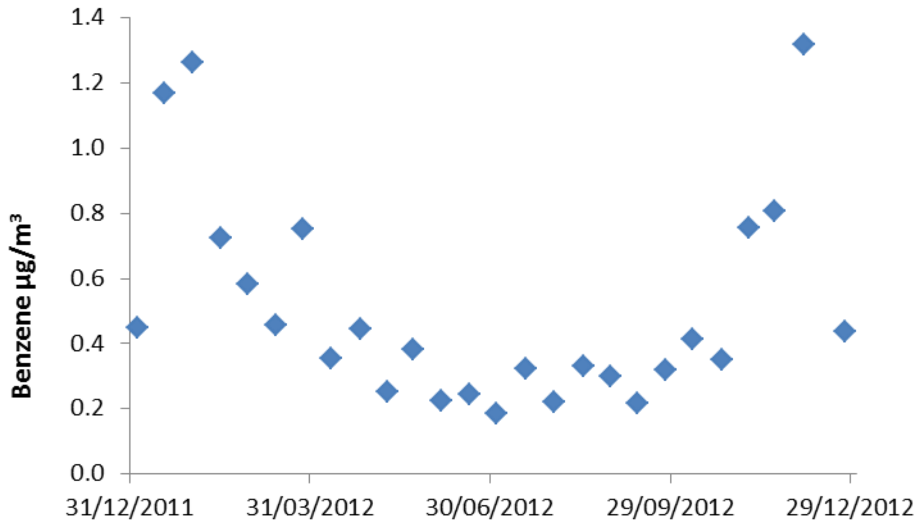


Figure 41 Glasgow Kerbside Non Automatic fortnightly Benzene

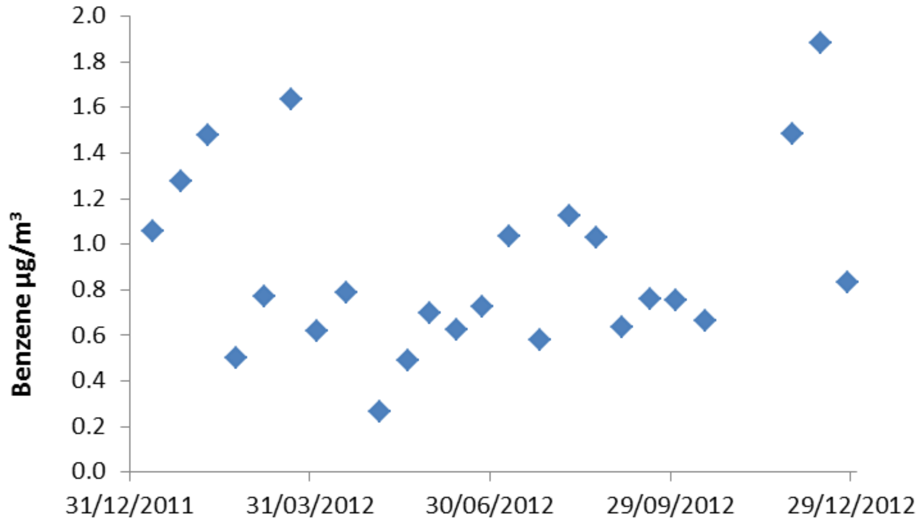
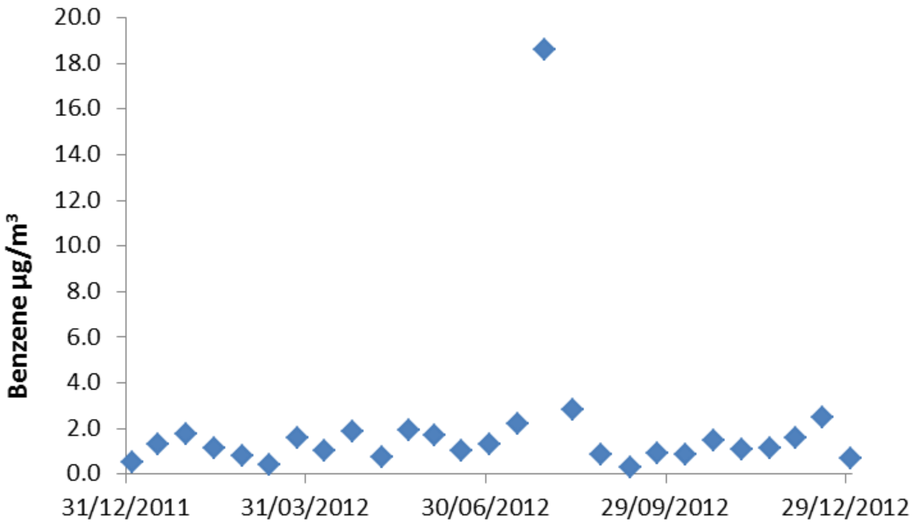


Figure 42 Grangemouth Non Automatic fortnightly Benzene



Note that there was a significantly elevated result in Grangemouth during July 2012 (Figure 39) and the data was correctly ratified. Upon investigation, the elevated levels at Grangemouth between 19th Julyand 3rd August 2012 were found to correspond to an incident at the Petroineos Plant petrochemical plant. It was reported that a collapsed roof to a stabilised gasoline tank occurred during this period and this is considered to be a major source of the high fortnightly measurement

Figure 43 Haringey Roadside Non Automatic fortnightly Benzene

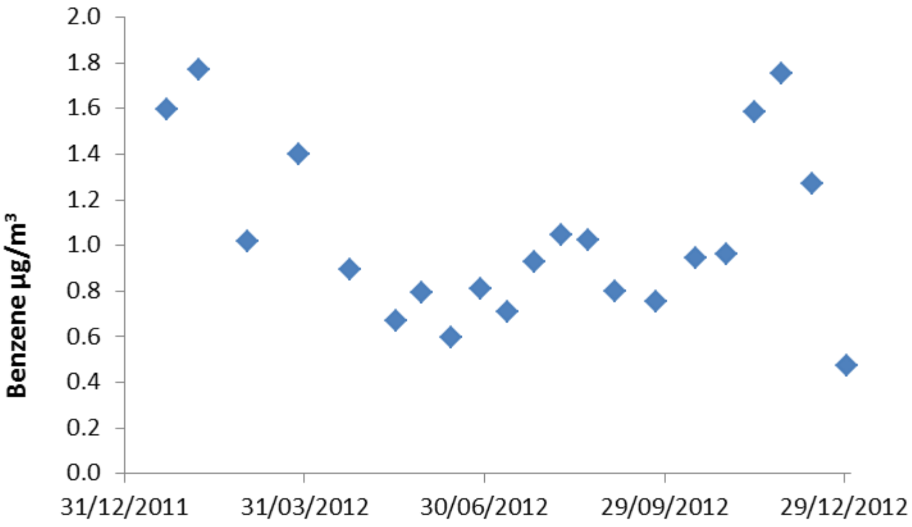


Figure 44 Leamington Spa Non Automatic fortnightly Benzene

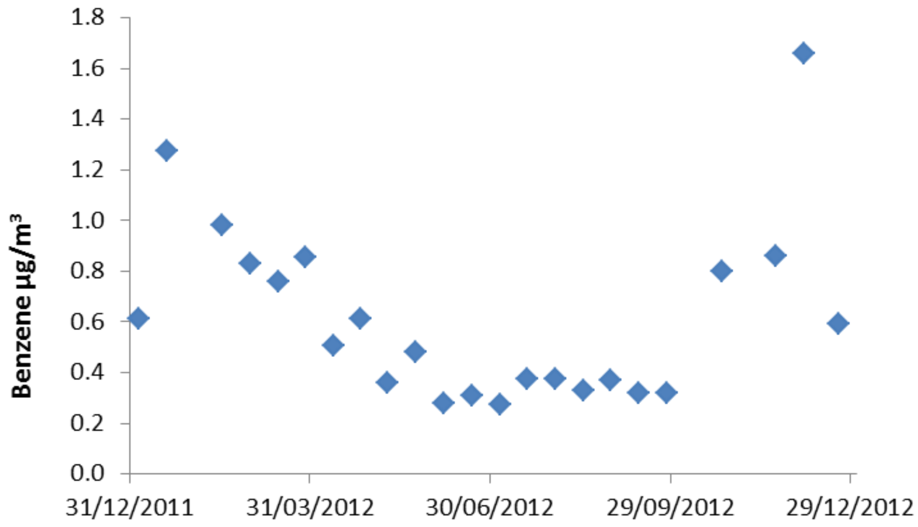


Figure 45 Leeds Centre Non Automatic fortnightly Benzene

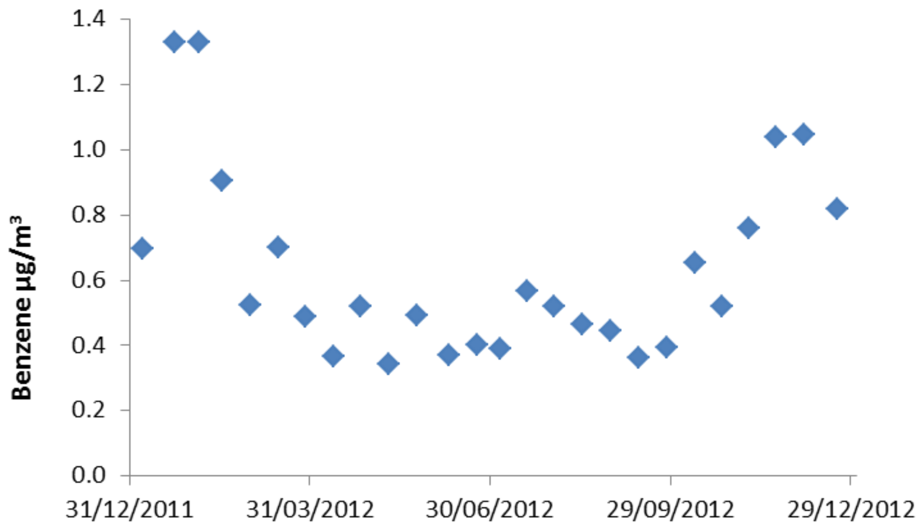


Figure 46 Leicester Centre Non Automatic fortnightly Benzene

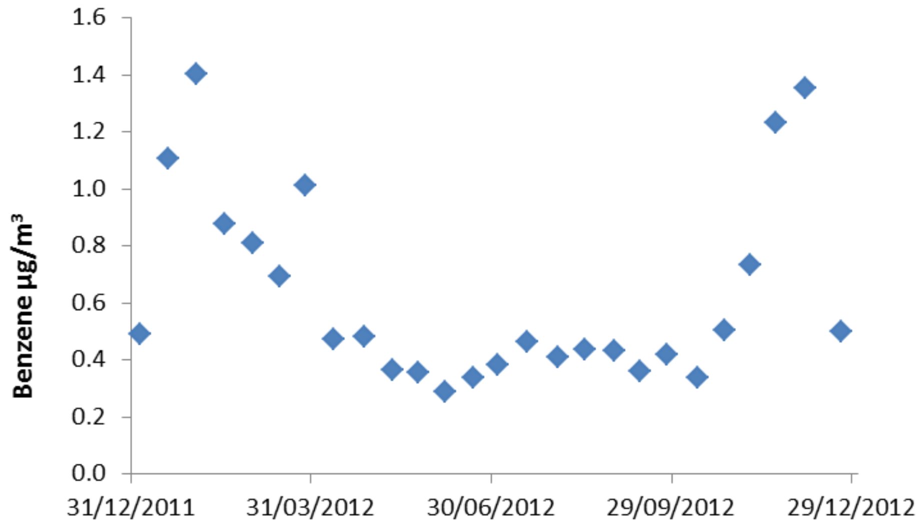


Figure 47 Liverpool Speke Non Automatic fortnightly Benzene

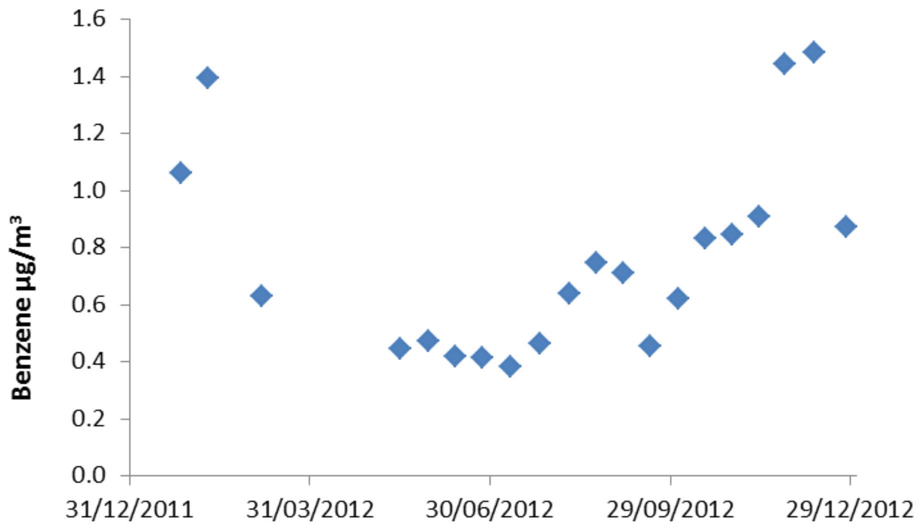


Figure 48 London Bloomsbury Non Automatic fortnightly Benzene

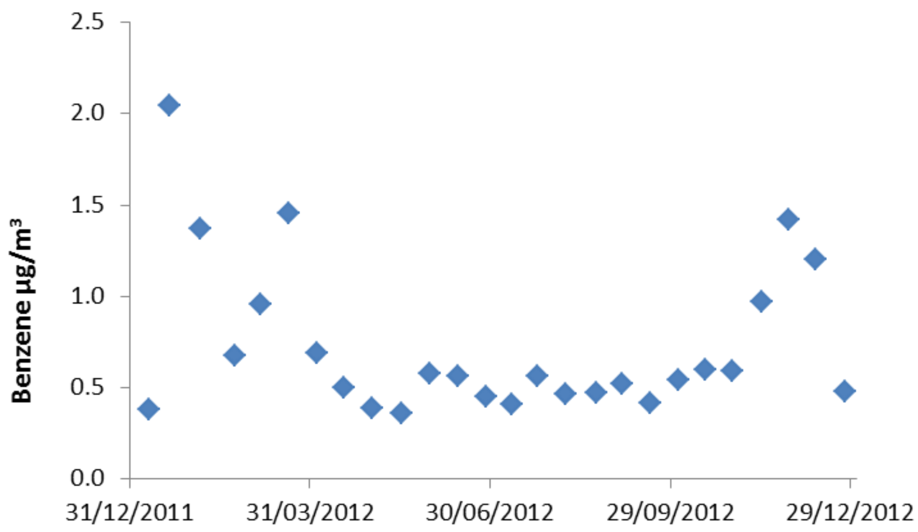


Figure 49 Manchester Piccadilly Non Automatic fortnightly Benzene

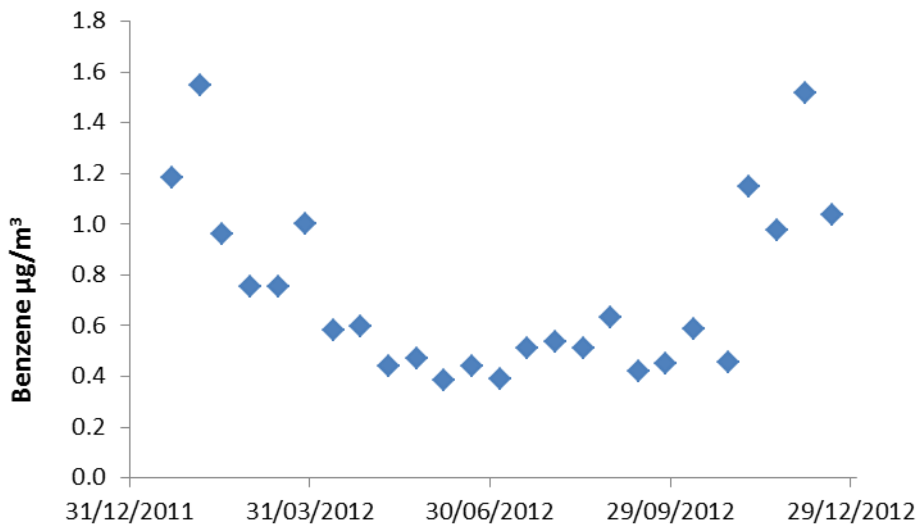


Figure 50 Middlesbrough Centre Non Automatic fortnightly Benzene

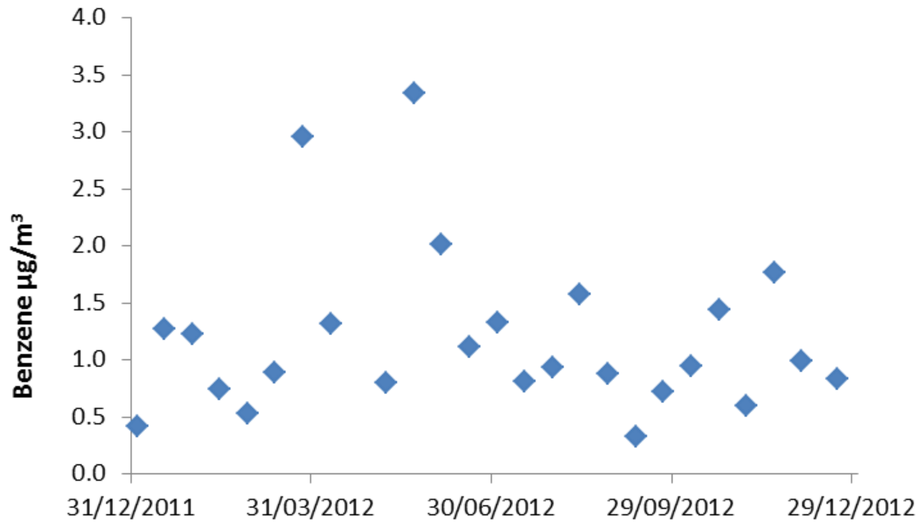


Figure 51 Newcastle Centre Non Automatic fortnightly Benzene

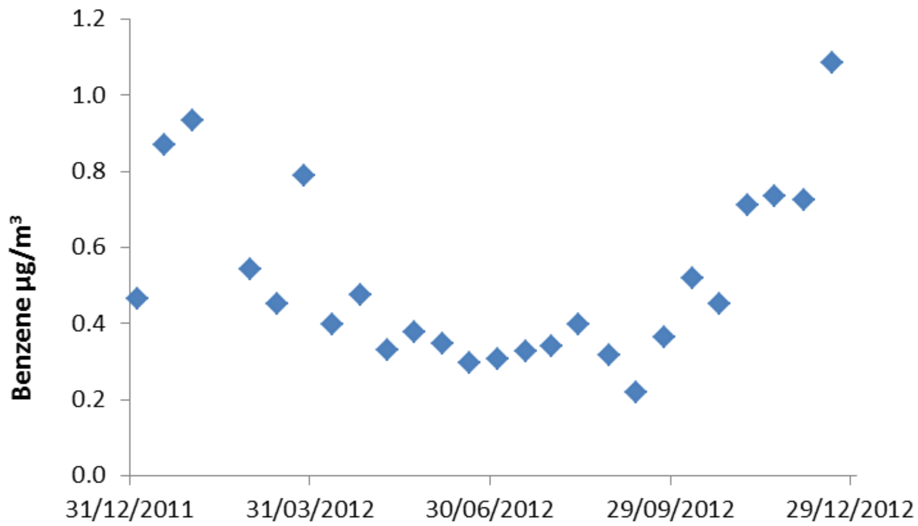


Figure 52   Northampton Non Automatic fortnightly Benzene

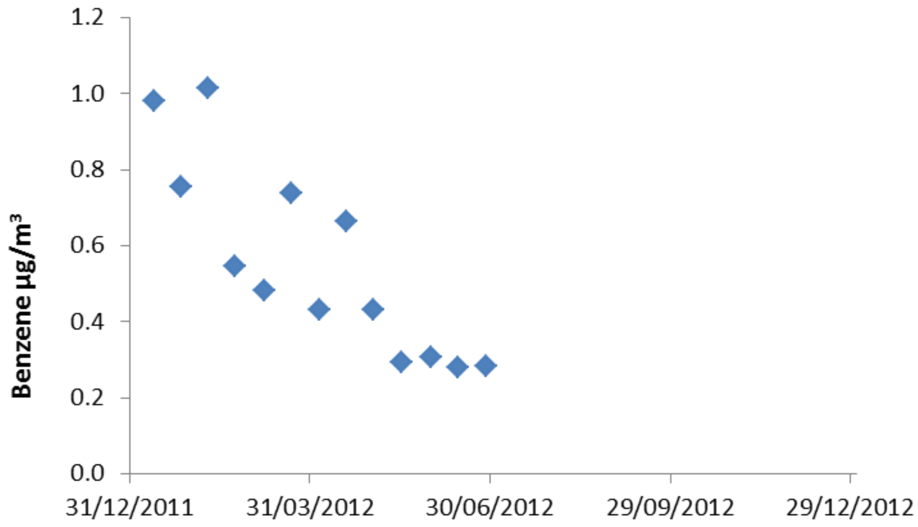


Figure 53   Norwich Lakenfields Non Automatic fortnightly Benzene

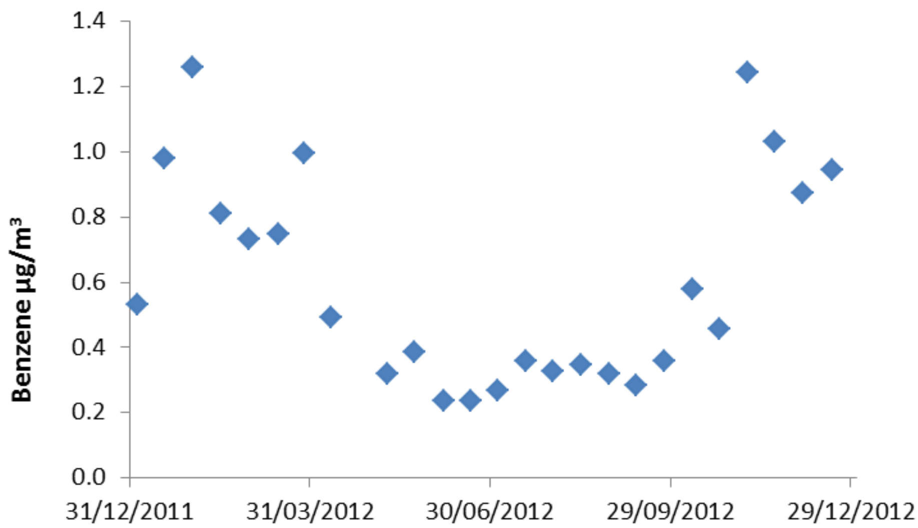


Figure 54 Nottingham Centre Non Automatic fortnightly Benzene

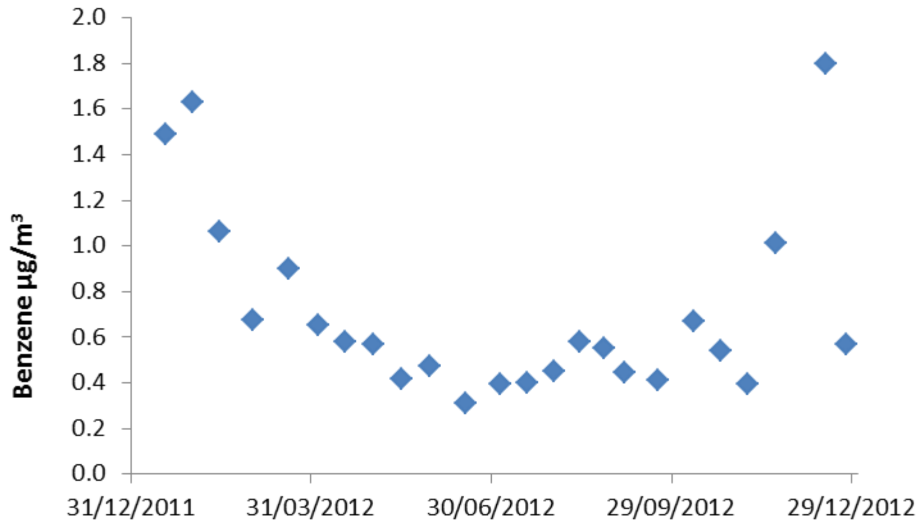


Figure 55 Oxford Centre Roadside Non Automatic fortnightly Benzene

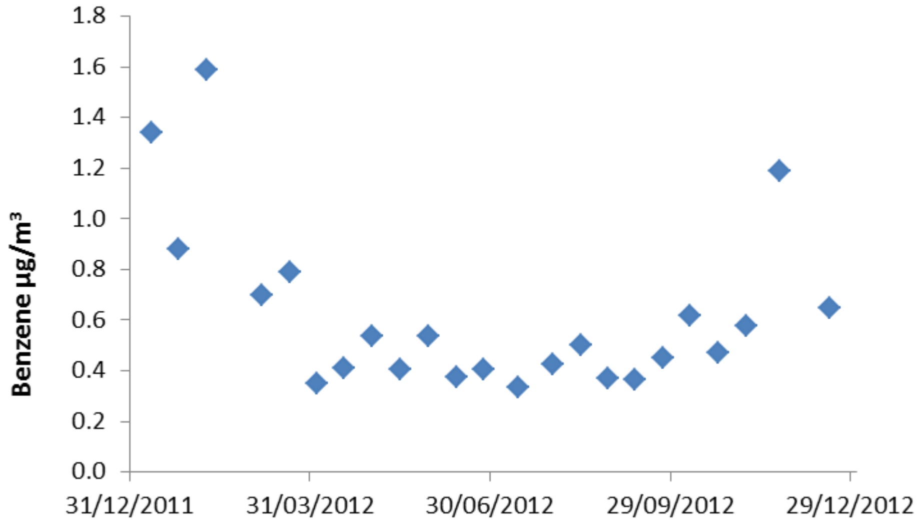


Figure 56 Oxford St Ebbes Non Automatic fortnightly Benzene

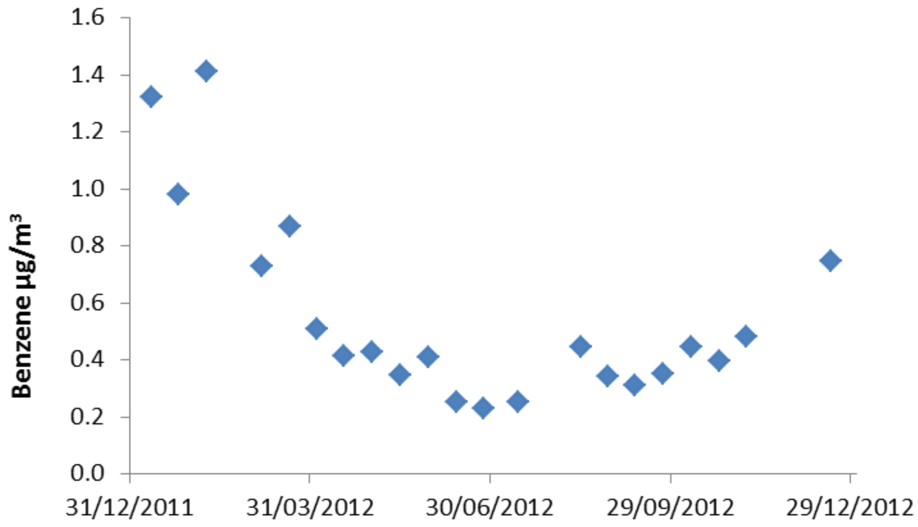


Figure 57 Plymouth Non Automatic fortnightly Benzene

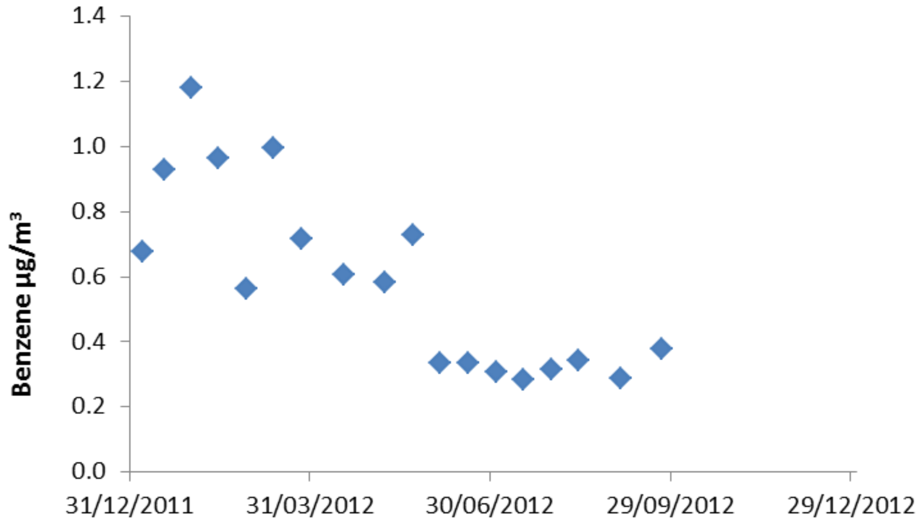


Figure 58   Sheffield Centre Non Automatic fortnightly Benzene

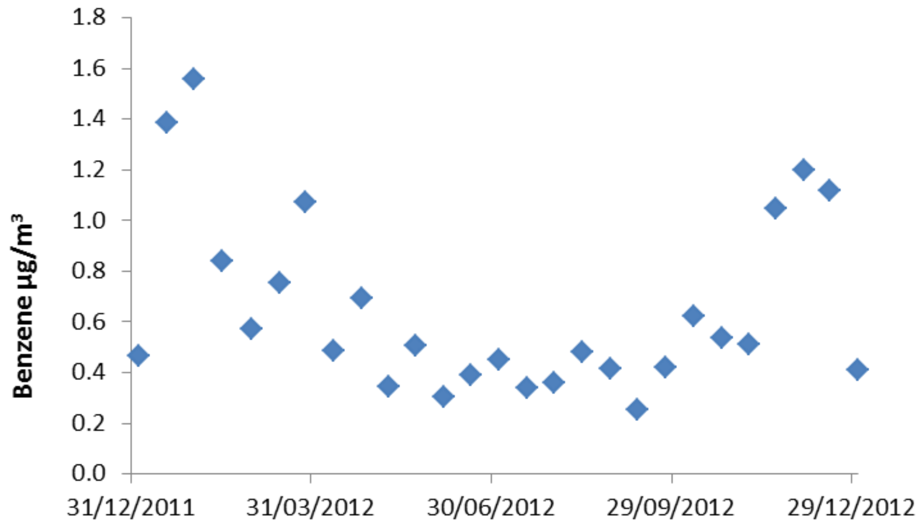


Figure 59   Southampton Non Automatic fortnightly Benzene

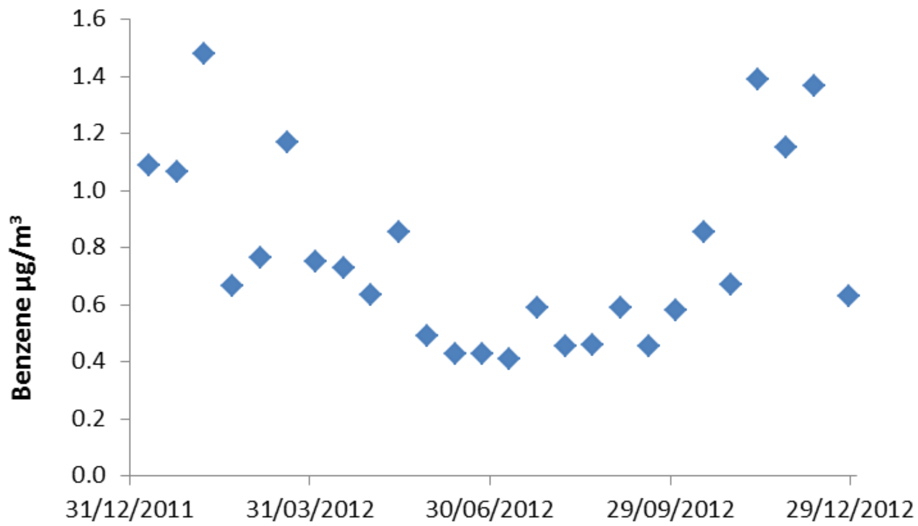


Figure 60   Stockton-on-Tees Eaglescliffe Non Automatic fortnightly Benzene

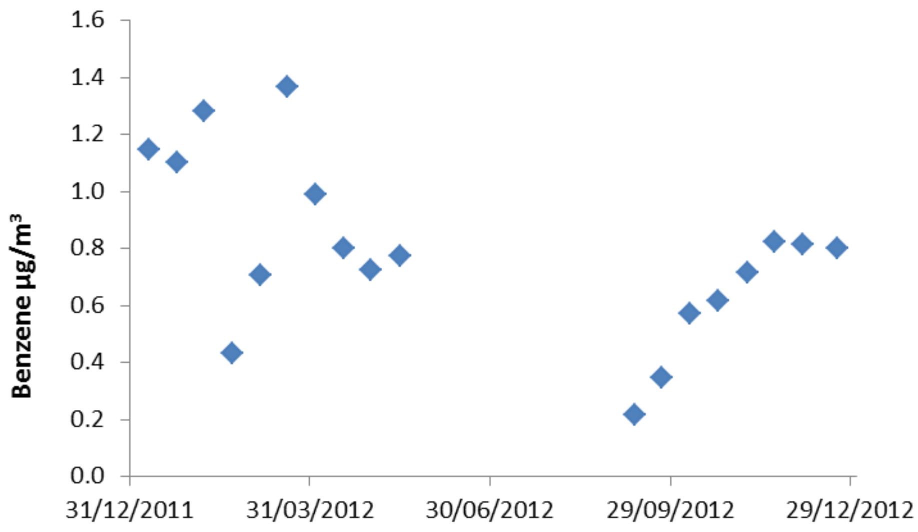


Figure 61   Stoke-on-Trent Centre Non Automatic fortnightly Benzene

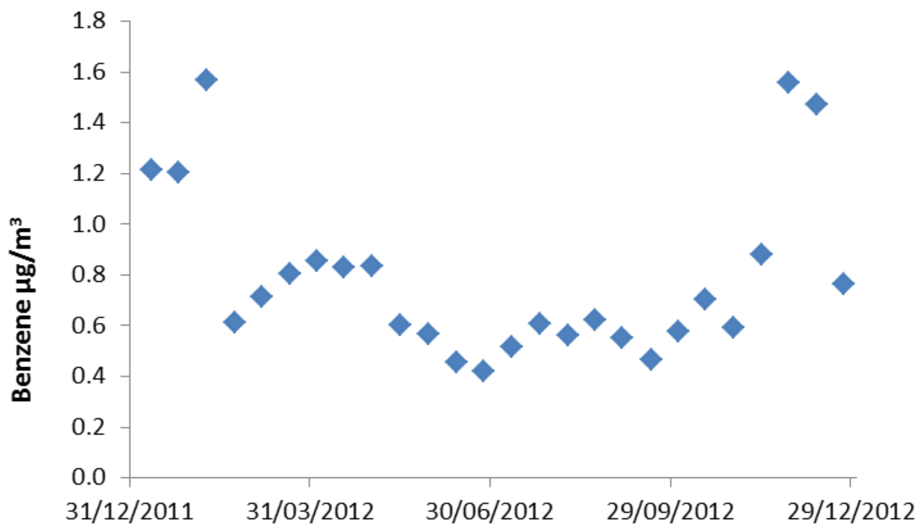


Figure 62 Wigan Centre Non Automatic fortnightly Benzene

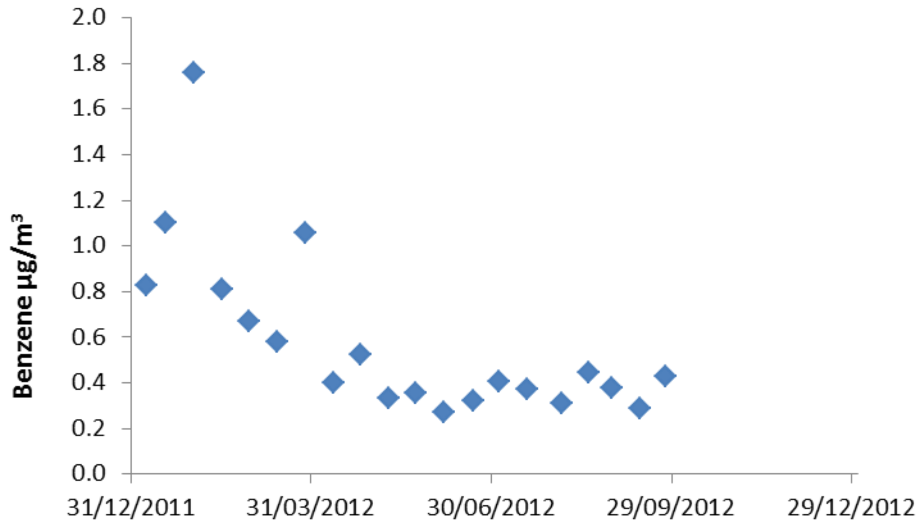
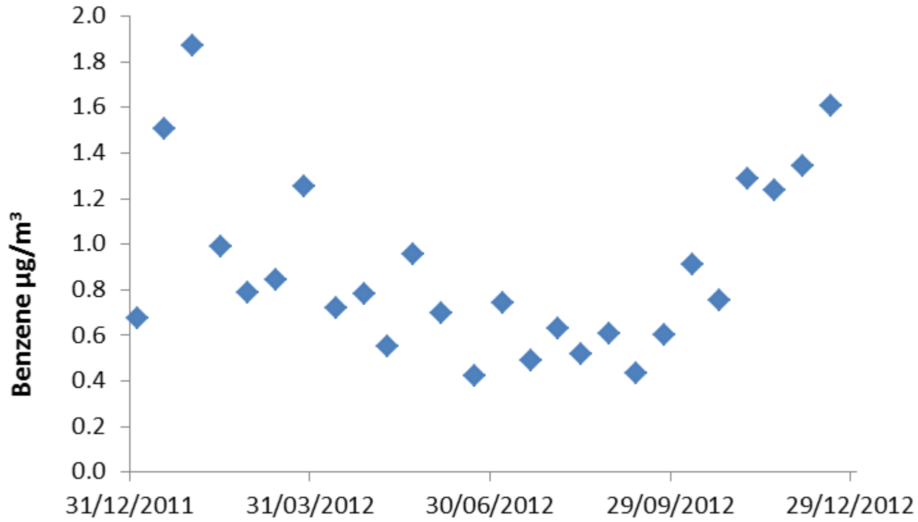


Figure 63 York Fishergate Non Automatic fortnightly Benzene



RICARDO-AEA

The Gemini Building
Fermi Avenue
Harwell
Didcot
Oxfordshire
OX11 0QR

Tel: 0870 190 1900
Fax: 0870 190 6318

www.ricardo-aea.com